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PATH DIFFERENCES WITHIN WHICH SPECTRUM INTERFERENCES ARE OBSERVABLE

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1. *Reflecting systems.*—Certain earlier results (Carnegie Publications, No. 249, 1916, §56) made it seem plausible that the path differences within which interferences are obtained (i.e., the *apparent* lengths of uniform wave trains) increase as the dispersion, to which the incident collimated white light (L figure 1) is subjected, is made continually greater. With this quest in view the aim is to produce the interferences by one and the same method, but with a successive variation of the dispersion of the spectra. The method (figure 1) was first selected for this purpose (M, N, P', mirrors; T, telescope; s,s', screens), inasmuch as the use of prisms or gratings of different dispersive power at P meets the requirements, while spectra of the first and second order are equally available.

In work of this kind the spectra must be bright; otherwise the fine lines will escape detection. Deficient values will thus be obtained if the spectra are too dark. Moreover the results can not furnish data of precision, since the exact instant at which fringes, continually decreasing in size, have actually vanished, can not be fixed; and it is the fine fringes which furnish a considerable amount of the displacement. The differences, however, are so large, that orders of values are apparent, more than sufficient to substantiate the argument.

It is possible that the method (figure 1) gives the half ranges only, since the efficient pencils of light, $C\,C'$, can not cross each other when M is displaced. The methods applied will nevertheless be trustworthy, since they are identical, the same telescope and other appurtenances

being used throughout. Later, the grating method is to be suitably modified for corroborative experiments.

The first series of measurements was obtained with a 60° prism at P, the dispersive power $d\theta/d\lambda$ being computed (approximately) from Cauchy's equation, so that in wave length λ

$$d\delta/d\lambda = 4B \sin \tfrac{1}{2}\varphi/\lambda^3 \cos \tfrac{1}{2}(\varphi + \delta),$$

φ being the prism angle (60°) and δ the angle of minimum deviation. The dispersion constant B was estimated to be 4.6×10^{-11}.

In the remaining series with a grating at P, $d\theta/d\lambda = 1/D \cos \theta$, the usual expression, θ being the angle of diffraction and D the grating space. The dispersive power thus increases from about 800 to 17,000, over twenty times. Throughout this whole enormous range good fringes were obtained.

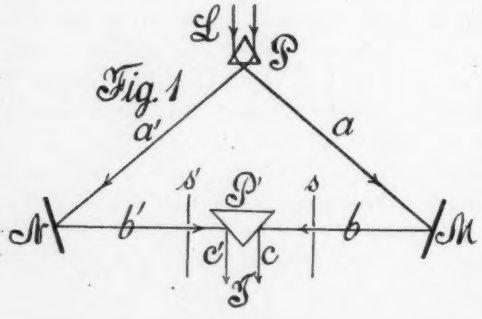


Fig. 1

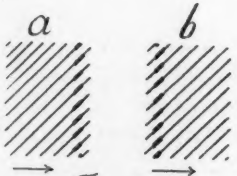


Fig. 2

The values, e, show the normal displacements of the opaque mirror M, during the presence of fringes, and of the opaque mirror N, as specified. Of these, e_M is systematically larger than e_N for reasons due to residual curvature in the mirrors and surfaces, whereby fringes on the left (N) vanish sooner than those on the right (M). The datum, y, is the displacement of the right angled reflecting prism P', parallel to the component rays bb'. This value is necessarily smaller than e, as will be shown elsewhere. All measurements were frequently repeated and the means finally taken for comparison with $d\theta/d\lambda$.

In the experiments with a ruled grating at P and a concave grating reflecting at P', the phenomenon of figure 2 was observed. A wide field of faint fringes was visible, enormously accentuated and clear in the narrow strip of the linear phenomenon. As the micrometer mirror at M moves forward, these faint fringes shift bodily across the stationary bright linear strip, beginning therefore with the pattern a

and ending with b. The faint fringes follow the rules of displacement interferometry.

TABLE 1

RANGE OF DISPLACEMENT, e, y, VARYING WITH DISPERSION

METHOD	$e_M \times 10^3$	$e_N \times 10^3$	$y \times 10^3$	θ	$d\theta/d\lambda$
	cm.	cm.	cm.		
60° prism at P	28	24	21	49°45′	760
Grating ($D = 352 \times 10^{-6}$) at P	161	136	108	9°39′	2,880
Same. 2d order	250	230	155	19°34′	6,030
Film grating ($D = 167 \times 10^{-6}$) at P	302	236	190	20°40′	6,400
Same. 2d order	470	420	440	44°56′	16,900

In addition to the data of the table, a large number of miscellaneous tests were made with the reflecting prism in different positions. Unless brought too far to the rear, when the beams are lost at the edge and e too small, the results for fine and coarser fringes were of the same order.

The data for e are not sufficiently regular in the dispersive powers above 1000 for graphic treatment (it is probable that at 16,900 the sliding along the prism surface is interfered with) but the data for the path difference, $2y$, are available. All the data, in consideration of their limitations, bear out the inference that the range of displacement within which fringes are seen, increases in marked degree with the dispersion, the average initial ratio $2y/(d\theta/d\lambda)$ is about 60×10^{-6} cm.

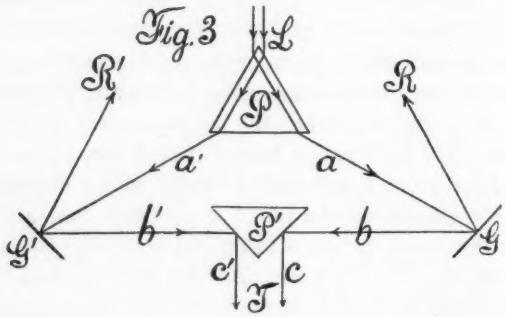
A very surprising result in these experiments is the efficiency of the film grating in series IV and V, not only in the first but in the second order of spectra.

After these experiments an attempt was made to obtain similar results with the more comprehensive method of two gratings G and G' (transmitting G at P and reflecting G' at P') with an appropriate change of the angle δ. But here the choice of gratings with satisfactory constants was limited and with high double dispersion the fields were apt to be too dark. Good results were obtained with the 60° prism and concave grating and with the ruled grating together with the latter. The data again showed marked increase of displacement with the dispersion $d\theta/d\lambda$.

2. *Diffraction at M, N, replacing reflection.*—The present method of observing interferences in the zeroth, first, second, third and even fourth order, successively, without essential change of the parts of the apparatus, is noteworthy. In figure 3, the incident light L from the collimator is separated into two component beams a and a' by the 60° prism, P. This is essential here, as an abundance of light is needed

(sunlight should be focused by a large lens of long focus—5 feet—on the slit). The rays a, a', are then either reflected or diffracted in any order, by the identical plane reflecting gratings G, G', into the collinear rays b, b'. These are reflected by the silvered right angled prism P' and observed in a telescope at T. G and G' and also P' should be on micrometers, so that the corresponding displacements, e, e', normal to G and G' and y in the direction $b\,b'$, may be registered.

The adjustments, if symmetry were demanded, would be cumbersome; for in addition to precise modification of the position and orienta-



tion of the prisms P, P', the grating requires fine adjustment and a means of securing parallelism of the rulings. But an approximate adjustment does very well and no pains were taken to secure symmetry. The spectra were brilliant in the low order work; but even in the fourth order the light was adequate. One may note that the gratings enhance the dispersion of the prism P, which is relatively small. Table 2 is an example of results.

TABLE 2

RANGES OF DISPLACEMENT, e, VARYING WITH DISPERSION. PAIRED GRATINGS (SPACE $D = 200 \times 10^{-6}$ cm) AND 60° Prism. $\theta = 46°, \delta = 44°$. PATH DIFFERENCE $x = 2e \cos \delta/2$

ORDER	OBSERVED		
	$e \times 10^3$	$x \times 10^3$	$d\theta/d\lambda$
	cm.	cm.	
0	38	70	760
1	190	350	3,490
2	420	780	6,440
3[1]	520	962	9,930
4[1]	580	1,070	14,800

[1] Fringes too faint.

The fringes in the zeroth order were good and strong not inferior to any of the others, but unfortunately too shortlived. In the fourth order the fringes are weak (although the enormous sodium doublets stand out clearly), doubtless from excess of extraneous light. Here also it is difficult to prevent the beam from vanishing at the edge of the prism P'. Hence the anomalously small displacement, a discrepancy already quite manifest in the third order.

The present experiments furnish a striking example of the uniform breadth of the strip of spectrum carrying the fringes, quite apart from the dispersion of the spectra. In the prism spectrum, where the sodium doublets are indicated by a hair line just visible, to the fourth order spectra, where they stand apart like ropes, the linear interference phenomenon has the same width.

The computation of the dispersive power in these cases is peculiar. It will be seen from figure 3, that the angle ($\delta = 44°$) between the incident ray a and the diffracted ray b is constant and is $\delta = \theta + i$ in the first and second and $\delta = \theta - i$ in the third and fourth order. Hence in succession (i changing sign after the 2d order)

$$\sin(\delta - i) - \sin i = \lambda/D,$$
$$\sin(\delta - i) - \sin i = 2\lambda/D, \text{ etc.},$$

from which equations the angle i may be computed. I did this with sufficient accuracy graphically.

Since $d\theta = di$, apart from sign, it follows that the dispersing power is

$$-d\theta/d\lambda = n/D\,(\cos i + \cos(\delta - i))$$

where n is the order of the spectrum. With the values of i given, the data for $d\theta/d\lambda$ were finally computed. The dispersive power of the prism was computed as above and is to be added to all the succeeding dispersive powers. The path difference, $x = 2e \cos \delta/2$ here corresponds to $2y$ above. Through the second order the rate $x/(d\theta/d\lambda)$ is about 120×10^{-6}. This value is larger than the former owing to incidental conditions. Similarly the proportionate effect of dispersion breaks down in the third and fourth orders, as already stated. The spectra themselves were still adequately bright, but the fringes were faint for some reason and I failed to make them stronger.

NON-REVERSED SPECTRA OF RESTRICTED COINCIDENCE

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In figure 1 the white ray L from the collimator is diffracted by the grating G and the two spectra a and a' thereafter reflected by the parallel opaque mirrors M and N, to be again diffracted by the grating G'. The rays are observed by a telescope at T. If the gratings, G, G' have the same constant, it is obvious that the field of the telescope will show a sharp white image of the slit, for each mirror. If M N G G' are adjusted for symmetry by aid of the adjustment screws on each and the rulings are parallel, the two white slit images will coincide horizontally and vertically. If now a direct vision spectroscopic prism, or a direct vision prism grating G'' is placed in front of the telescope, the superposed white slit images will be drawn out into overlapping non-reversed spectra, which will usually show a broad strip of interference fringes.[1]

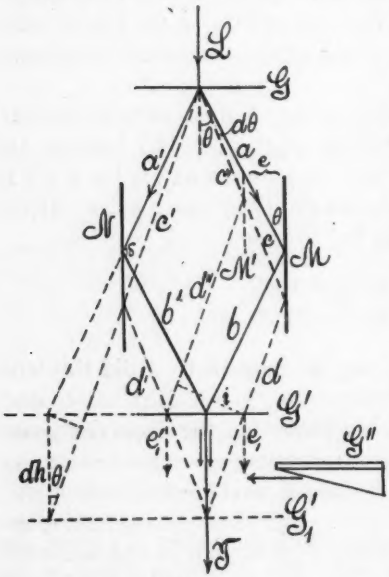

FIG. 1.

When first found, the fringes were very fine parallel lines, filling an irregular strip in the orange-yellow region, and it was already obvious that an enormous play of the micrometer screw at M would be permissible.

A number of film gratings were tested and the best samples selected ($D = 175 \times 10^{-6}$), although the dispersion was still too large and the D lines not clear. To secure more light, a beam of sunlight 15 cm. in diameter was condensed to a focus on the slit by a large lens of about 2 meters in focal distance. The illumination was now adequate and the fringes were found at once. These fringes, in view of more accurate adjustment, were also larger than before.

Figure 1 shows, if ab, $a'b'$ and cd, $c'd'$ are pairs of corresponding rays

of the same order but different wave lengths, λ and λ', respectively, that for the given position of G and G', only the rays $a\ a'$ issue coincidently at T. The rays cd, $c'd'$ issue at e_1, e'_1 and though brought to the identical focus by the telescope, the distance $e_1\ e'_1$ may be too large to admit of appreciable interference. Hence the colored strip within which interferences occur will comprise those wave lengths which lie very near λ, whereas the colors lying near λ', etc., will be free from interference.

If the mirror M is displaced parallel to itself to M' by the micrometer screw, the rays $c''\ d''$, and $c'\ d'$ will now coincide at e'_1, whereas the rays from $a\ b$ and $a'b'$ will no longer issue coincidently and may not interfere. Thus the interferences are transferred as a group from rays lying near λ to rays lying near λ'. It is obvious therefore that with the displacement of M, the strip carrying interferences will shift through the spectrum and that a relatively enormous play of the micrometer slide at M will be available without the loss of interferences. In fact a displacement, e, of over 3 cm. of M normal to itself, produced no appreciable change in the size or form of fringes, but they passed from the green region into the red. The fringes as seen with a fine slit were straight parallel strong lines. They did not thin out to hair lines at their ends, nor show curvature, as one would be inclined to anticipate. On the contrary, they terminated rather abruptly at the edges of a strip occupying about one-fourth of the visible length of the spectrum.

It follows, from figure 1, that the displacement of M does not change the lengths of rays; for they are enclosed between parallel planes, as it were. Since the double angle of reflection is here $\delta = 180° - 2\theta$, where θ is the angle of diffraction of G and G', the displacements of M over a normal distance e will shorten the path at M in accordance with the equation

$$n\lambda = 2e \cos \delta/2 = 2e \sin \theta \qquad (1)$$

where n is the number of fringes passing at wave length λ.

This equation[2] is not obvious, as for constant λ, the distance between G and G' measured along a given ray, for any position of M or N, is also constant. The equation may be corroborated by drawing the diffracted wave front i for instance, which cuts off a length $2e \sin \theta$ from d''.

Since $\sin \theta = \lambda/D$ if D is the grating space, the last equation becomes

$$n = 2e/D$$

or per fringe

$$\delta e = D/2,$$

a remarkable result, showing that the displacement of the mirror M per fringe is independent of wave length and equal to half the grating space. An interferometer independent of λ and available throughout relatively enormous ranges of displacement is thus at hand. It appears that it is also independent of the angle of incidence at G.

In case of the given grating and sodium light $\theta = 19° 37'$. Hence if δe is the displacement per fringe[2]

$$e = \lambda/2 \sin \theta = 10^{-6} \times 88 \text{ cm.}$$

Actuating the micrometer at M directly by hand the following rough data were successively obtained from displacements corresponding to 10 fringes:

$$10^6 \times \delta e = 65 \quad 95 \quad 90 \quad 80 \quad 60 \text{ cm.}$$

Without special precaution the fine fringes can not be counted closer than this, so that the data are corroborative.

The fore and aft motion of G' produces no separate shift of fringes while the fringe bearing strip is displaced as a whole in mean wave length. Figure 1 shows at once that if G' were displaced to G'_1, the λ rays $b\,b'$ would lose their coincidence in T, while that property would now be possessed by the λ' rays $d\,d'$. But the same path difference is added to both d and d'. The ratio of corresponding displacements at M and G' is $\tan \theta : 1$. Equation (1) is of interest in interferometry, in view of the very long ranges of displacements available. For such purposes gratings of lower dispersion (preferably ruled gratings or else prisms) may be used to obtain greater luminous intensity in the spectrum. Path difference may also be introduced by compensators. If a thin sheet of mica is moved in either b or b' there is a lively skirmish of fringes, but they do not change size appreciably. A plate 2.8 millimeters thick with strong fringes horizontal in the yellow, if placed in the b' pencil produces hair lines inclined toward the left in the red; if placed in the b pencil, hair lines inclined to the left in the green; etc. Plates were tested up to 2 cm. To fully exhibit their effect it is necessary to produce the elliptic fringes, presently to be referred to. The shift from red to green, if produced without compensators by the displacement of M, shows scarcely any variation of fringes, either as to size or inclination.

To change the size of fringes it is easiest to rotate the grating G' (relatively to G) on a horizontal axis normal to itself. They then both rotate and grow coarser, usually attaining the maximum of size when the fringes are vertical. Fringes quite large and black may be obtained

in this way, which are naturally much more sensitive. Size may also be changed by compensators and this method is usually more available.

In addition to the above experiments, work was done at some length with homogeneous light, with gratings of different constants, etc., which cannot be detailed here. The most interesting result was obtained with a *wide* slit and white light. It was shown that the fringes are ultimately nearly confocal ellipses of enormous eccentricity and with the major axis vertical. To produce and center them, the refraction (dispersion) of plates is advantageous, if not necessary.

It is now of interest to turn to the displacement of G', normal to itself, and to consider the resolving power of the system. For the latter bears a close analogy to the experiments made in a preceding paper. (Carnegie Publication, No. 249, § 37 et. seq., 1916) on the behavior of crossed rays. If G' is displaced to G'_1, over a distance $e' = dh$ (see figure 1 where h is the distance apart of G and G'), the rays λ' meeting in T will now be in the same condition as were originally the rays λ. In other words, e'_1 and e'_1 have become coincident at G'. If we assume that rotationally the same type of fringe results in these cases, and if $\lambda' - \lambda = d\lambda$, $\theta - \theta' = d\theta$, (for the passage of bb' into dd' is in the direction from red to violet)

$$d\theta = dh \sin\theta \cos\theta/h, \qquad \text{nearly.}$$

Since $\lambda = D \sin\theta$ and $d\lambda = -D \cos\theta\, d\theta$, this may be changed to

$$d\lambda/\lambda = dh\,(1 - \lambda^2/D^2)/h$$

when D is the grating constant.

The present method, apart from any practical outcome, is worth pursuing because of the data it will furnish of the width of the strip of spectrum carrying interference fringes, under any given conditions. For here the spectra are not reversed or inverted and the latitude of interference or diffraction throughout λ is much broader than in case of reversed spectra. But for this purpose films will not suffice and rigid refracting systems must be devised, and the grating constants must be quite identical.

[1] This article is a note from a Report to the Carnegie Institution of Washington.

[2] The equation is also true for oblique incidence. But for this and the use of homogeneous light with a wide slit, the availability of gratings of different constants, etc., the report mentioned may be consulted.

THE EQUILIBRIUM BETWEEN ACIDS AND BASES IN SEA WATER

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The alkaline reaction of sea water and the chemical equilibria that define it concern not only the oceanographer but also the geologist and the biologist. For information upon this subject must lead to further knowledge regarding geographical variations in the composition of the sea, the chemical reactions which have taken place during the existence of the ocean, the present movements of carbonic acid upon the earth, and the environmental relations of sea water to marine flora and fauna.

In the present investigation it has been sought, first, to determine the influence of carbon dioxide tension and of salinity upon the hydrogen ion concentration of sea water and, secondly, to construct a solution of exactly known composition, which shall reproduce the behavior of sea water when subjected to changes in carbonic acid concentration. This task has been accomplished with such accuracy as existing methods of investigation afford. The results define the acid-base relation between marine organisms and their environment, the fluctuations in this relationship, and the means by which such fluctuations are controlled. They also yield evidence concerning the geological history of the ocean. When combined with the observations of Palitzsch, they lead to a general description of the geographical variation in the chemical equilibria of sea water and to information concerning the gradients along which carbon dioxide is at present moving in the sea and in the air.

1. *Hydrogen Ion Concentration and Carbon Dioxide Tension of Sea Water.*—A large number of estimations of the hydrogen ion concentration of sea water, when saturated with carbon dioxide at tensions between 0 and 760 mm., have been made. The hydrogen ion concentrations were determined colorimetrically, following exactly the procedure of Palitzsch,[1] and at first with his kind assistance,[2] so that the results are strictly comparable with his. The standard solutions were in all cases analyzed with the hydrogen electrode. Carbon dioxide tensions, after equilibrium had been established, were determined either by chemical analysis of the gas phase or with the manometer. The following table corresponds to the curve which best fits the data of these experiments.

Salinity per cent	Temperature degrees	Hydrogen ion concentration	CO_2 tension mm.
31.92	20± 1	135 × 10^{-7}	760
31.92	20± 1	121 × 10^{-7}	700
31.92	20± 1	112 × 10^{-7}	600
31.92	20± 1	93 × 10^{-7}	500
31.92	20± 1	76 × 10^{-7}	400
31.92	20± 1	55 × 10^{-7}	300
31.92	20± 1	36.2 × 10^{-7}	200
31.92	20± 1	17.0 × 10^{-7}	100
31.92	20± 1	12.1 × 10^{-7}	75
31.92	20± 1	8.7 × 10^{-7}	50
32.45	20± 1	5.24 × 10^{-7}	25
32.45	20± 1	2.19 × 10^{-7}	10
32.45	20± 1	1.74 × 10^{-7}	7.5
32.45	20± 1	1.20 × 10^{-7}	5.0
32.45	20± 1	0.66 × 10^{-7}	2.5
32.45	20± 1	0.27 × 10^{-7}	1.0
32.45	20± 1	0.195 × 10^{-7}	0.75
32.45	20± 1	0.121 × 10^{-7}	0.5
32.45	20± 1	0.078 × 10^{-7}	0.25
32.45	20± 1	0.057 × 10^{-7}	0.1

2. *Effect of Salinity upon the Hydrogen Ion Concentration of Sea Waters at the same Carbon Dioxide Tension.*—Such variations of salinity as occur in the sea, although they do not ordinarily sensibly affect the proportions of the several components, must obviously exert a certain influence upon the hydrogen ion concentration. The following data indicate approximately the magnitude of this effect.

Number	Depth	Salinity	CO_2 tension mm.	Hydrogen ion concentration
10313	20 meters	30.73	0.3	0.093 × 10^{-7}
10301		31.58	0.3	0.087 × 10^{-7}
10305		32.05	0.3	0.085 × 10^{-7}
10305		32.34	0.3	0.085 × 10^{-7}
1000	20 ft.	32.45	0.3	0.087 × 10^{-7}
10299	210 meters	33.62	0.3	0.081 × 10^{-7}
10304		34.16	0.3	0.083 × 10^{-7}
10288	225 meters	34.60	0.3	0.079 × 10^{-7}

3. *Effect of Temperature upon the Hydrogen Ion Concentration of Sea Water.*—A more important effect upon hydrogen ion concentration is exerted by the temperature. This depends, first, upon the change in the absorption coefficient of the gas with change of temperature and, secondly, upon a simultaneous change in the ionization constants of the several substances involved in the equilibrium. Certain observations upon the apparent hydrogen ion concentrations of sea water at different temperatures, to which no value as quantitative estimations can at

present be attached, illustrate the general character of this effect, which is dependent mainly upon the first factor mentioned above.

Temperature degrees	*Salinity*	*Hydrogen ion concentration*
0	32.45	0.141×10^{-7}
10	32.45	0.107×10^{-7}
20	32.45	0.085×10^{-7}
30	32.45	0.060×10^{-7}
40	32.45	0.0446×10^{-7}

These measurements indicate that under ordinary circumstances, when unaffected by the products of metabolism or the constituents of river water, the reaction of the sea water is fully determined by (1) the tension of carbonic acid, (2) the concentration of water, or salinity, and (3) the temperature. This relationship suggests a method of determining the carbon dioxide tension of sea water, which will be published later.

4. *Hydrogen Ion Concentration of Natural and Artificial Sea Water.*—So far as the acid-base equilibrium is concerned, sea water may be exactly imitated by a system consisting only of water and sodium chloride together with carbonic acid, and boric or silicic acid, partly combined with alkali. Thus, if a solution be prepared containing

NaCl	35.0 g. per liter
Na_2CO_3	0.1035 g. per liter
H_3BO_3	0.0620 g. per liter
$Na_2B_4O_7$	0.0253 g. per liter

and set up in series with sea water of salinity 32.45, the two systems, after saturation with carbon dioxide at *any* tension between 0 and 760 mm., will possess the same hydrogen ion concentration, as estimated by indicators. This result, however, in that it is comparative, eliminates all estimations of the acidity of the solution. And accordingly the most trustworthy result of the present investigation is proof of the equivalence, in respect to hydrogen ion concentration, of sea water with this artificial system containing boric acid in a concentration 0.0015 molal, carbonic acid in an amount determined by the tension of its gas, and a single base in a concentration 0.0022 molal, distributed between boric and carbonic acids.

It is now evident that the ocean, which, because of the presence of free carbonic acid, was originally acid, and which has been becoming more alkaline from the accumulation of basic material, is at present in an epoch where the growing alkalinity is checked by the *buffer* action of acids of approximately the strength of boric acid. These acids are prob-

ably chiefly silicic acid and boric acid, though the conversion of bicarbonates into carbonates is also of importance.

These buffers regulate the reaction of sea water at the present time in a manner quite similar to the way in which bicarbonates and phosphates regulate the reaction of blood. The principal effect of the products of metabolism upon sea water is defined by the data concerning variation in the carbon dioxide tension.

5. *Geographical Variation in Carbon Dioxide Tension.*—Taking account of the facts as stated above, certain conclusions regarding geographical variations in the composition of sea water may be deduced from Palitzsch's data.

First, the uniform increase in acidity of sea water with increase of depth, proves that the concentration of free carbonic acid everywhere varies in like manner. This may be illustrated by one example.

Station 81.

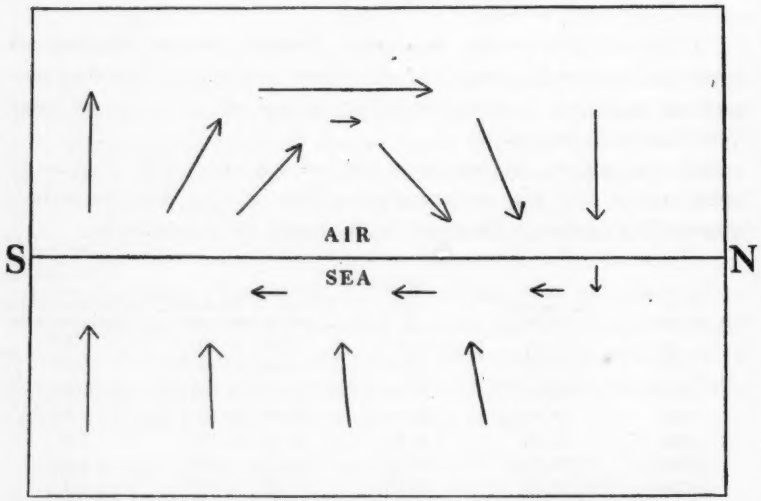
Depth meters	*Temperature in situ*	*Salinity %*	*Hydrogen ion concentration at room temperature*	*Relative concentration of free carbonic acid*
0	17.94	35.43	0.060×10^{-7}	1.0
50	13.56	35.52	0.066×10^{-7}	1.3
100	12.56	35.63	0.074×10^{-7}	1.8
400	11.01	35.57	0.091×10^{-7}	2.5
800	11.25	36.02	0.098×10^{-7}	2.8
1000	10.84	36.02	0.098×10^{-7}	2.8
1200	9.89	36.00	0.104×10^{-7}	3.1
1500	6.97	35.50	0.112×10^{-7}	3.4
2000	4.20	35.10	0.112×10^{-7}	3.4

Disregarding a conceivable effect of pressure, it seems to follow from these facts that, upon the whole, (i.e., in most places and at most seasons) carbonic acid is escaping from the sea into the air.

Secondly, the well marked variation in hydrogen ion concentration with latitude and therefore according to the temperature, in the case of surface waters, indicates that the concentration of free carbonic acid at the surface steadily increases in the direction of the pole. This, no doubt, depends upon the variation of the absorption coefficient of the gas with change in temperature. And, taking account of Krogh's[3] observations upon the high tensions of carbon dioxide, and the uniformly greater tension of atmospheric than of surface carbon dioxide in high latitudes, it appears to be certain that in cold marine regions carbonic acid is passing from air to sea. It does not appear likely that this absorption of carbon dioxide by the cold oceans can balance its escape from the warm oceans, first, because Palitzsch found, even in cold regions, an increase of hydrogen ion concentration with the depth, and,

secondly, because in the Mediterranean, where no deep arctic current flows, carbonic acid is escaping from the sea.

The special features of this movement of carbon dioxide can only be discovered through very extensive investigations, but its general character seems to be indicated by the following diagram.



MOVEMENTS OF CARBON DIOXIDE IN A VERTICAL NORTH-SOUTH PLANE, IN THE NORTHERN HEMISPHERE

These results afford one more instance of similarity between regulatory processes in the organism and in the environment.

We are greatly indebted to Dr. Palitzsch for furthering this investigation by his invaluable advice.

[1] Sven Palitzsch, Measurements of the hydrogen ion concentration in sea water, *Report on the Danish Oceanographical Expeditions 1908–10 to the Mediterranean and Adjacent Seas*, vol. 1, p. 237.

[2] During the early part of this investigation Dr. Palitzsch, as *Scandinavian Scholar*, was at work in the Gibbs Laboratory.

[3] August Krogh, The abnormal CO_2 percentage in the air in Greenland and the general relations between atmospheric and oceanic carbonic acid, *Meddelelser om. Grönland*, No. 25–26, p. 434, 1904.

AN APPARENT CORRESPONDENCE BETWEEN THE CHEMISTRY OF IGNEOUS MAGMAS AND OF ORGANIC METABOLISM

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In a recent paper[1] it was shown that potassium and magnesium on the one hand, and sodium and iron on the other, tend to vary together in igneous magmas and the minerals formed from them. That is, igneous rocks and minerals which are high in potassium contain, (of the two), much magnesium and but little iron; while if the rock or mineral is dominantly sodic iron will be high and magnesium low, if these are present. This relation seems to be independent of the silicity (amount of silica) and but slightly modified by the amount of calcium.

The object of the present note is to call attention to what appears to be a congruous relation of these pairs of elements in the organic world —briefly stated, it would appear that, of the four, iron and sodium are necessary for animal metabolism, (magnesium and potassium very much less so); while magnesium and potassium are essential to vegetable metabolism, the other pair being of minor importance.

This correspondence is indicated by the following considerations, all of which are well-known to biologists, so that it is only in their collocation and the pointing out of an apparent congruity in the chemistry of the mineral with the animal and vegetable kindgoms that there is any novelty.

It is well-known that the blood pigments of the higher animals, hemoglobin and its congeners and derivatives, are protein bodies which contain iron as an essential constituent, and it has been suggested[2] that this element acts as the oxygen carrier in the vital processes in which the blood plays the all-important part. In the blood plasma sodium is an important constituent, its amount being several times that of the potassium, though the latter element is, apparently, more important in the cells. The amount of magnesium in the plasma is also very small.

As stated by one authority[3] it would appear that "potassium compounds are replaced in the [animal] organism by sodium chloride," and that as a consequence "common salt is, not only a condiment, but a necessary addition to the food." The universal and necessary use of sodium chloride in food by man and many of the higher animals need only be mentioned.

In plants, on the other hand, the active metabolic agent which enables the organism to assimilate carbon from the CO_2 of the atmosphere is chlorophyll, and it is now well-known through recent researches[4] that this is a protein compound which contains magnesium as an essential constituent. In this connection it is of especial interest to note that chlorophyll is very closely related chemically to hemoglobin, the formulae and apparently the constitution of the two being almost identical;[5] except that the animal metabolic agent is an iron compound and the vegetable agent is one of magnesium, and that the former contains slightly more oxygen than the latter. In this similarity we are reminded of the association and mutual isomorphous replaceability of iron and magnesium among minerals.

In plants again, in contradistinction to animals, of the two alkali metals, "potassium, unlike sodium, is essential to plant life."[6] Water culture experiments have abundantly proved that, of the cations potassium, magnesium, and calcium are necessary to plant life, though a small amount of iron is requisite to the formation of chlorophyll, in which connection the close similarity between this substance and hemoglobin becomes of special interest. Sodium is not necessary to most plant existence.

Although of subsidiary importance, the relative toxicity of the several cations to animal and vegetable life is of interest, as bearing in the same way as the facts set forth above. It must, of course, be understood that toxicity is largely a matter of concentration and that we have to deal, here very briefly and inadequately, with the *relative* toxicities of approximately similar concentrations of the several elements. It is also to be understood that we shall consider only the four cations (Fe, Na, Mg, K), which here concern us, and disregard others, as Ca, as well as the anions or acid radicals.

To the animal organism the magnesium salts appear to be mildly toxic, or at least are very readily eliminated when ingested into the system, which is only true of the iron salts when taken in much greater amounts. That potassium is largely replaced in the animal organism by sodium has already been noted, and experiments by Loeb[7] and others, which can be but barely alluded to here, show that to many animal organisms potassium is distinctly toxic, its ill effects being neutralized by immersion in solutions of sodium salts.

To the higher plants, at least, the iron salts, especially those of ferrous[8] iron, are distinctly toxic when present in the soil in much more than the small amounts needed for its (possibly catalytic) action in the formation

of chlorophyll. Likewise sodium salts are, especially relatively to those of potsssium, decidedly toxic toward most vegetable life, though some plants, even of the highest genera, have become halophytic and have adapted themselves to soils and waters containing relatively large concentrations of sodium salts. Even in these, however, it would appear that potassium is the one of the alkali elements necessary to the plant's existence.

Briefly put, therefore, these relations of activity and toxicity of the two pairs of salts are antagonistic in the two kingdoms; that which is active in metabolism and chiefly necessary for life in the animal being relatively toxic in the vegetable, and vice versa.

Finally it may be pointed out that, according to Reichert,[9] hemoglobin is entirely absent from the lower orders of animals, such as the protozoa, porifera and coelenterata, is rare in the echinodermata, and that chlorophyll is present in some of these, as the protozoa. Thus it might almost be suggested that the nearer the animal organism approaches the vegetable the less the influence of iron and the greater that of magnesium in assimilative metabolism.

The facts thus very briefly and imperfectly set forth seem consistently and collectively to lead to the conclusion that, in general, of the four elements discussed, iron and sodium are, relatively to the other two, jointly necessary to animal metabolism and existence, while, per contra, magnesium and potassium replace them as essentials for plant life. Here we have, then, though opposed in the two types of organic metabolism, the same congruity between the two pairs of elements that has been shown to exist in minerals and igneous magmas. Whether this apparent state of affairs is merely coincidental and due to such external factors as conditions of environment, or whether it is based on some fundamental chemical characters or relations of the elements involved, can not be adequately discussed here.

Thus it might be argued in favor of the first supposition that the presence of abundant sodium in the blood plasma is due to the fact that this may represent the sea water in which the present day animal's ancestors once lived; that the presence of iron in the blood pigments may be ascribed to the existence of this element in two valencies, ferric and ferrous iron, and their ready transformation from one state of oxidation to the other;[10] that the presence of potassium rather than sodium in plants may reasonably be connected with the greater resistance to decomposition and greater insolubility of the potassium than the sodium minerals, and the consequent greater tendency of the former to accumulate in soils; and, lastly, that the fact that chlorophyll is a magnesium

compound may be correlated with the ability of this element to act as it does in Grignard's reaction, as has been suggested by Willstätter.[11] The relatively greater toxicity of potassium over sodium, as in Loeb's experiments with Fundulus, may be ascribed to selective absorption or membrane permeability. The connection between these pairs of elements in magmas and minerals may be ascribed to differences in solubility.

Each one of these or other such explanations, taken individually and separately, may be rational and valid; but taken collectively, especially in view of the congruity of the four elements in the mineral and organic kingdoms, they make it appear possible and indeed reasonable to ascribe the correspondence to some fundamental chemical relation between the elements involved, of which such proximate causal nexuses as have been suggested are the consequences. No hypothesis can be offered as to what may be the nature of this relation; only the mere possibility of its existence, based on the correspondences set forth in this and the preceding paper, can be suggested.

[1] H. S. Washington, these PROCEEDINGS, 1, 574 (1915).

[2] Cf. Reichert and Brown, *Carnegie Inst. Publ.*, No. 116, 24 (1909).

[3] O. Hamarsten (Transl. by Mandel), *Textbook of Physiological Chemistry*, p. 564 (1900).

[4] Cf. S. B. Schryver, *Science Progress*, 3, 440 (1909).

[5] Reichert and Brown, op. cit., 1; Schryver, op. cit., 444.

[6] E. Strasburger et al. (transl. by Porter), *Text-book of Botany*, 173 (1898).

[7] Cf. J. Loeb these PROCEEDINGS, 1, 473 (1915); 2, 511 (1916).

[8] It is suggested that the lesser toxicity of the ferric salts may be ascribed to their ready hydrolysis and the consequent formation of very difficultly soluble basic compounds.

[9] Op. cit., 2.

[10] Copper, likewise with two valencies, exists in the blood of certain lower animals, as mollusca, limulus, helix and sepia.

[11] The dependence of plant life on magnesium and of animal life on iron, and the difference in their functions, is expressed by Willstätter as follows: "There are fundamentally two kinds of life, which develop alongside of each other; the anabolic life with magnesium and the katabolic life (of animals) with iron, that is a reducing and an oxidizing life." *See Liebig's Ann. Chem.*, 250, 65 (1906).

THE OAKS OF AMERICA

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For a number of years I have been engaged in a study of the oaks of tropical America. These have not been treated comparatively for a generation, with the result that the extensive collections made within that time have gone into herbaria largely unnamed or wrongly named.

My feeling has been that the only way to unravel the difficulties was to begin with the study of types of the earlier species, passing to those of later date and deferring examination of unauthentic collections until the end. Though it was not possible to carry this plan out in all detail, it has been my privilege to see most of the types of tropical American species, and to photograph in natural size representative parts of them whenever found, so that whatever errors may have slipped in, they scarcely include a misapprehension as to what is meant by the earlier used names except for one or two of Née's species of which no identifiable material is known to remain.

It was not until this study of the forms that occur to the south of us had been essentially finished, that it seemed best to include in my treatment those of the United States. These have been so long and so repeatedly studied and for the most part figured that little would seem to have been left undone with them. Yet within the year Professor Sargent has pointed out a serious misapprehension as to the proper Latin names of the rock chestnut oak and the cow oak, and has made it very questionable whether what we know as red oak in the northern States is what Linnaeus called *Quercus rubra*. As I finish my manuscript, in which for completeness the northern oaks are included summarily, I have a feeling that more uncertainty still attends several of these polymorphic species than perhaps any one which occurs in the tropics; and unfortunately this uncertainty for the most part cannot be removed by reference to types, which do not exist for the most puzzling of these northern species.

A careful analysis of the characters presented by wood, inflorescence and flowers leads me to believe that the Fagaceae are far from being the primitive plants that they are commonly taken for, and I am disposed to conclude that their affinities are with such seemingly advanced and certainly specialized but still really simple orders as the Ranunculales and Rosales, from the type of which they have receded.

On this continent, the oaks (excluding *Pasania* as a distinctly separable genus) seem to fall into three subgenera or main groups instead of two as usually understood, Leucobalanus, the white oaks, typical of *Quercus;* Erythrobalanus, the red or black oaks; and Protobalanus, a more ancient type as I conceive it, comprising the protean intermediate assemblage clustering about *Q. chrysolepis*.

Summarized, my study of American materials contained in the principal herbaria of the world leads to the recognition of 354 species, of which 158, or very nearly one-half, are described as new in the manuscript which I am now prepared to submit to the Academy for publi-

cation, in which 183, or slightly over one-half of the whole, are figured for the first time. As in our immediate flora, white and red oaks occur in approximately equal numbers for the American flora as a whole: 170 species of the former, and 179 of the latter, only 4 species of Protobalanus being known.

In variety as well as in actual number of species, the countries to the south of us are much richer in oaks than the Atlantic United States—a result to be expected from the more rugged configuration and greater meteorologic differences in those countries. The principal facts of the distribution of American oaks by countries are indicated in the following table. A very few species occur in more than one country, and therefore are counted for both.

COUNTRY	LEUCOBALANUS	PROTOBALANUS	ERYTHROBALANUS	TOTAL
United States	43	2	26	71
Mexico	121	2	125	248
Central America	20	0	35	55
South America	0	0	4	4
Antilles	1	0	0	1
Pacific Islands	0	1	0	1

A glance at this table shows that, rich as the United States are in oaks, they are nearly equaled by the small Central American countries and far surpassed by Mexico. In the West Indies only a single species of white oak, doubtfully distinct from the live oak of our Gulf States, occurs, and this unquestionably derived from our mainland. In South America there are only four closely related species, of the red oak group, and these are clearly allied with some of the Costa Rican species.

The genus *Quercus* is conceded to have existed in Cretaceous time though many Cretaceous and Tertiary fossils formerly referred to this genus are now placed in *Dryophyllum*, which is taken for the ancestral stock of the Fagaceae rather than of *Quercus* alone. Paleobotanists now admit 150 species of American fossil oaks pretty evenly distributed through the Cretaceous and the Eocene and Miocene divisions of the Tertiary. Few Pliocene fossils are known for North America; but in South America where a few others have been made known for the Argentine, 4 species have been described from Pliocene deposits of equatorial Brazil. It is noteworthy that the few existing South American oaks are confined to the Andes of Colombia.

So far as I know, none of the earlier species survived from one to another of the periods of geologic time except for *Q. furcinervis americana*

(perhaps two distinct species) in Eocene and Miocene deposits, and that what has been taken for the existing *Q. chrysolepis*—the type of the subgenus Protobalanus—occurred in the Miocene; but this identification might well be questioned by a critic. A proper understanding of the affinities of existing groups of species undoubtedly calls for a just appreciation of their connection with these ancestral forms. This I do not profess to have formed. I find the occurrence of a few aberrants—among them the South American species—in the subgenus Erythrobalanus puzzling, but can see no satisfactory evidence that red- or black-oaks are recognizable in any of the older fossils; and the group is certainly exclusively American today. Notwithstanding this, a resemblance is observable between the white oaks of Europe and those of western rather than eastern America, that proves puzzling.

On the whole, I am unable to trace any existing groups to those of Tertiary time. Pleistocene species, of which 18 are recognized for the United States, as is to be expected are scarcely different from those of today, though they are sometimes given distinctive names. In the early Pliocene should be sought definitely recognizable ancestral forms of these and their living descendants.

Considering the multitudinous—and in their extremes very diverse—types of such an existing assemblage as that of the Rocky Mountains, in which Engelmann and other excellent botanists have been unable to see more than a single polymorphic species, and the comparable range—to which the keen von Ettingshausen refers the manifold European oak types of today—in the fossil *Q. Palaeo-Ilex*, I am unable to see that all of the existing American oaks may not have descended from a single synthetic type of this kind, such as the Miocene species that has been held to be identical with the existing intermediate oak *Q. chrysolepis*. Out of this type, rightly or wrongly, I have built the present divergent branches of white and red oaks as I understand their affinities, believing that the European and American white oaks have no direct connection and that on each continent the manifold and often parallel forms of today have been independently derived from distinct late Tertiary types not closely related to one another in descent.

A SET OF INDEPENDENT POSTULATES FOR CYCLIC ORDER

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There are four types of order which are important in geometry and other branches of mathematics: (1a) linear order with a definite sense along the line (theory of *serial order*); (1b) linear order without distinction of sense (theory of *betweenness*); (2a) circular order with a definite sense around the circle (theory of *cyclic order*); and (2b) circular order without distinction of sense (theory of *separation of pairs of points*).

The present note is concerned with type (2a): cyclic order.

Let us consider a *class* K of elements $A, B, C, \ldots$, and a *triadic relation* $R(ABC)$. The class K may be said to be *cyclically ordered* by the relation R if the following postulates are satisfied:

I. *If A, B, C, are distinct, then ABC implies BCA.*

II. *If A, B, C are distinct, then at least one of the orders ABC, BCA, CAB, CBA, ACB, BAC is true.*

III. *If A, B, C are distinct, then ABC and ACB cannot both be true.*

IV. *If ABC is true, then A, B, and C are distinct.*

V. *If A, B, X, Y are distinct, and XAB and AYB, then XAY.*

From these postulates it follows that any three distinct elements A, B, C, in the order ABC, divide the class into three sections, such that (1) the three sections, together with the dividing elements, exhaust the class; (2) no element belongs to more than one section; (3) if X, Y, Z are elements taken one from each section, so that AXB and BYC and CZA, then XYZ. The details of the proof will be given in a later paper.

It will also be shown that the postulates are independent of each other.

From I, II, and V we can prove, as a theorem,

VI. *If A, B, X, Y are distinct, and AXB and AYB, then either AXY or YXB.*

But if we should replace postulate I by the following postulate:

I′. *If A, B, C are distinct, then ABC implies CBA,*

then VI would become an independent postulate, and the set of six postulates, I′, II, III, IV, V, VI, would then define not cyclic order, but

betweenness, and would be, in fact, identical with one of the sets of independent postulates for betweenness obtained in a forthcoming paper by E. V. Huntington and J. R. Kline. The transition from the theory of cyclic order to the theory of betweenness may thus be made by merely interchanging two letters in the first postulate; postulates II–VI are true in both theories.

A NEW METHOD OF STUDYING IDEATIONAL AND ALLIED FORMS OF BEHAVIOR IN MAN AND OTHER ANIMALS[1]

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Despite widespread interest in the evolution of reasoning, the comparative study of ideational behavior has been neglected. Only a few methods of research have been devised, and these have seen scant service.

Thorndike[2] is responsible for the problem or puzzle-box method (used by him in the study of cats, dogs, and monkeys); Hamilton,[3] for the method of quadruple choices (by which he has studied cats, dogs, horses, monkeys, rats, gophers, and men); Hunter,[4] for the method of delayed reaction (applied by him to rats, raccoons, dogs, and children).

I have perfected and applied a new method—that of multiple choices—for the detection of reactive tendencies and the study of their rôle in the attempted solution of certain types of problem. The method involves the presentation to the subject of a problem or series of problems whose rapid and complete solution depends upon ideational processes.

The apparatus consists of twelve, or, in some forms, nine identical reaction-mechanisms, of which any number may be used for a given experimental observation. In the type of apparatus originally used for human subjects, these mechanisms are simple keys; in that which has been used for lower animals, they are boxes arranged side by side, each with an entrance door at one end and an exit door at the other, which may be raised or lowered at need by the experimenter through the use of a system of weighted cords. Under the exit door of each box is a receptacle in which some form of reward for correct reaction may be concealed until the door of the appropriate box is raised by the experimenter.

It is the task of the subject to select from any group of these boxes whose entrance doors are raised that one in which the reward (food, for example) is to be presented. The experimenter in advance defines the

correct box for any group of boxes which may be used as that which bears a certain definite spatial or numerical relation to the other members of its group. Definitions which have actually been employed (problems presented) are the following: (1) the first box at the left end of the group (as faced by the subject); (2) the second box from the right end of the group; (3) alternately, the box at the left end and the box at the right end of the group; (4) the middle box of the group.

The boxes are presented in varying groups in accordance with a prearranged plan. The subject is punished by confinement in the box selected every time it makes an incorrect choice and is then allowed to choose again, and so on until it finally selects that box which is by definition the correct one. It is then rewarded with food and permitted to pass through the box and return to the starting point, where it awaits opportunity to respond to a new group.

The experimenter keeps a precise record of the subject's choices and of various important aspects of behavior. These data include the nature of the choices from trial to trial, series to series, day to day; the appearance and fate of specific reactive tendencies or methods of attempting to solve a problem; and the final outcome, in success or failure, of prolonged effort.

The essential statistical features of the results obtained with certain types of subject may be summarized briefly thus:

(1) Crows quickly solve problem 1 (first mechanism at one end of the group), with 50 to 100 trials.

Problem 2 (second from the end) they fail to solve in 500 trials. No consistent improvement appears, although there are four conspicuous reactive tendencies: (a) to go to the end box because of previous training in problem 1; (b) to go to the first box at the left and then to the one next in order, which in the particular experiment happened to be the correct one; (this is the most nearly adequate tendency exhibited by the crow); (c) to reënter whichever box happened to be chosen first and to choose next the second box from the left (correct); (d) to enter a box at or near the right end of a group, and on emerging, to turn to the right and enter the box directly in front, and so on until the correct box is located.

In the method of multiple choices, the crow gives no convincing evidence of ideational behavior. Its general intelligence is clearly indicated by alertness, keenness of perception, emotional responsiveness, and rapid adjustment to various essential features of the experimental situation. It appears to be temperamentally ill-suited to the kind of task presented by this method of studying reactive tendencies.

(2) White rats solve problem 1 in from 170 to 350 trials on the basis

of certain acquired motor tendencies, one of which may be described thus. The rat follows the wall of the reaction compartment to the entrance to the box at the right end of the series of boxes. It then turns sharply to the left and passes along close to the boxes until the first open door is reached. This it enters. Kinaesthetic, tactual, and visual data constitute the basis for the motor habits by which rats solve this simple relational problem.

A single individual exhibited reactive tendencies less obviously describable in motor terms, but it is by no means certain that this indicates ideational ability sufficient for the solution of relational problems.

Problem 2 was not solved by rats within 800 trials, and there is no indication in the data that solution is possible to them.

Whereas the influence of training in problem 1 disappeared quickly when problem 2 was presented to the crow, it persisted in the case of the rat for about 100 trials. There are numerous other evidences, in the experimental data, of the higher intelligence of the crow. The rat is distinctly less versatile and markedly less responsive to slight changes in environment.

(3) Pigs solve problem 1 with 50 trials or less; problem 2 with 390 to 600 trials; problem 3 with 420 to 470 trials. Problem 4 is not solved in 800 trials.

These successes as well as the varied reactive tendencies manifested place the pig much higher in the scale of adaptive capacity than the rat or crow.

The data obtained with these three types of subject proves the method of multiple choices to be a feasible means of eliciting reactive tendencies which are characteristic of various points in ontogeny and phylogeny.

Results which have been obtained with monkeys, apes, and men will be presented in separate communications.

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ELECTRICAL CONDUCTION IN DILUTE AMALGAMS

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The modern theory of electrical conduction in metals, according to which the metal is dissociated to give a positive ion of low mobility, which is characteristic of the metal, and a negative carrier of high mobility, which is common to all metals and presumably to be identified with the electron, has given rise to certain misgivings, despite the complete analogy between this theory and the accepted theory of electrolytic dissociation. It is true that in the case of solid metals the crystalline forces, which lead to the formation of the various components of the metal into symmetrical space-lattices, produce conditions which have no counterpart in liquid electrolytes, but in the case of a liquid metal like mercury we must assume that it differs from any electrolyte —we are tempted to say from any other electrolyte—only in as far as one of its ions has properties which differ very greatly in degree, but probably not in kind, from the properties of other ions. If therefore we should ultimately find that the Arrhenius theory of ionization is not applicable to a liquid metal we should be inclined to believe that it is not completely valid in the case of electrolytes.

This theory of electrolytic dissociation, which was originally proposed to explain the properties of aqueous salt solutions, has since been successfully applied without essential modification to many types of non-aqueous solution. Moreover the extremely important work of Kraus,[1] which unfortunately has not yet been published in full, demonstrates the applicability of the same theory to solutions of metals in non-metallic solvents. Thus, when metallic sodium dissolves in liquid ammonia, he shows conclusively that it dissociates into sodium ions and into electrons which, like other ions, are to a considerable extent combined with the molecules of the solvent.

Since therefore the theory of ionization has been successfully applied to electrolytes and to solutions of metals in electrolytes, it seems desirable to attempt a further extension of these ideas by several methods to solutions of metals in metallic solvents, in particular to solutions of the alkali metals in liquid mercury, and thus eventually to pure mercury itself. It has been shown by Lewis, Adams, and Lanman[2] that the transference of matter with the electric current, which had previously been regarded as a distinguishing characteristic of electrolytic conductors, can be detected and measured in sodium and potassium amal-

gams. It is to be hoped that further knowledge of the transference numbers so obtained, together with accurate information concerning the electrical conductivity of amalgams, may furnish important evidence as to the nature of electrical conduction in dilute amalgams and in pure mercury.

Important investigations of the conductivity of amalgams and liquid alloys have been conducted by Bornemann and his collaborators,[3] but they have confined their studies to high concentrations. If from transference number and conductivity we propose to obtain information concerning the nature of the carriers in the amalgams and in pure mercury, analogous to that which has been derived from a similar study of aqueous solutions, we may expect the most significant results from an investigation of dilute amalgams, ranging from zero to one atom per cent. We shall describe in this paper the results of an investigation of the conductivity of dilute amalgams of sodium, potassium, and lithium.

Since the conductivity of these amalgams differs but little from that of pure mercury, the difference itself can be determined with accuracy only by methods of the highest precision. By means of a simple potentiometer method it was found possible to compare the conductivity of an amalgam with that of pure mercury with an accuracy of two or three parts in one hundred thousand. (Full details of the potentiometer method, together with the method of preparing, transferring and analyzing the amalgams, are contained in a paper which will shortly be offered for publication in the *Journal of the American Chemical Society*.)

The experimental results are given in the three following tables, in each of which the first column gives the atom per cent of alkali metal, and the second the specific resistance divided by that of pure mercury at the same temperature. The measurements were all made at about 20°C.

TABLE I
LITHIUM AMALGAM

ATOM PER CENT	RESISTANCE REFERRED TO MERCURY
0.03269	0.999468
0.09988	0.998280
0.3080	0.994006
0.4844	0.990105
0.7103	0.985603
0.8221	0.983097

TABLE II
SODIUM AMALGAM

ATOM PER CENT	RESISTANCE REFERRED TO MERCURY
0.09325	1.00071
0.2905	1.00204
0.3851	1.00274
0.8646	1.00535
1.197	1.00657
1.670	1.00800
2.113	1.00867
2.409	1.00893
2.644	1.00824
3.661	1.00657
4.916	1.00621

TABLE III
POTASSIUM AMALGAM

ATOM PER CENT	RESISTANCE REFERRED TO MERCURY
0.05831	1.00220
0.1791	1.00574
0.4068	1.01767
0.5590	1.02623
0.6502	1.03032
0.8777	1.04147
1.186	1.05341

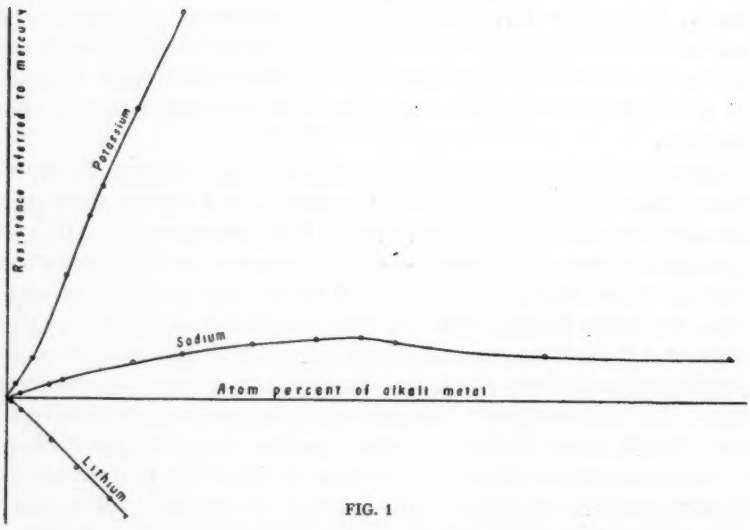

FIG. 1

The extraordinary difference between the three types of amalgam is shown in figure 1, from which it will be seen that a small addition of potassium increases the resistance of mercury, an equivalent amount of sodium produces a less increase in the resistance, while the addition of lithium diminishes the resistance.

It might have been expected, at first sight at least, that in accordance with the theory of electrolytic dissociation the strongly electropositive alkali metals would, owing to a greater dissociation, increase the conductivity of mercury. But when we consider the well substantiated fact that all these metals are, when dissolved in mercury, combined with the solvent to form hydrargyrates of greater or less complexity, the results cannot be considered to disprove this theory. Nevertheless it is important to observe that in interpreting the conductivity and transference number of dilute amalgams, the generalizations which can be drawn and the analogies which suggest themselves are of a very different character from those which have been found useful in the interpretation of the phenomena of aqueous solutions.

Thus in the paper of Lewis, Adams, and Lanman it has been shown that, contrary to expectation, the strongly electropositive metals sodium and potassium, when dissolved in mercury, wander in the direction not of the positive but of the negative current. They show further that this phenomenon is closely correlated with the increase in resistance produced in mercury by the solution of these metals; for if the in-

creased resistance be ascribed to a greater resistance to the motion of the electron in those regions of the mercury which contain particles of the dissolved metal, these particles or regions, according to the law of action and reaction, will be impelled in the direction in which the electrons are moving. This explanation is borne out by the fact that potassium, which produces a greater increase in the resistance of mercury than an equivalent amount of sodium, is also transferred to a greater extent in the direction of the negative current.

We may also suggest here another relationship of considerable interest. Attention has been called by Kraus[4] to the very large influence upon the conductivity of liquid mercury of a change of volume through pressure. Now it has been shown by Maey[5] that the addition of the alkali metals produces a very considerable change in the volume of mercury. This change in volume follows the same order as the electrical resistance of the amalgams given in the preceding tables. It is interesting therefore to see how the resistance of mercury would change upon the addition of the three alkali metals, if this addition were made, not at constant pressure, but with such change of pressure as would keep constant the average atomic volume, that is, the volume occupied by 1 gram of solvent and solute together.

If R is the resistance of pure mercury, V and V' the atomic volumes respectively of pure mercury and of amalgams, P the pressure in kilograms per square centimeter, and N the atomic fraction of the dissolved metal, then, according to the measurements of Bridgman,[6] $d\ln R/dP = -3.34 \times 10^{-5}$, while from the measurements of Richards, of Buchanan, and of Bridgman,[7] $d\ln V/dP = -3.8 \times 10^{-6}$. Hence $d\ln R/d\ln V = 8.79$. In Table IV the second column gives the value of $d\ln V'/dN$ calculated from the work of Maey, and the third column the values of $d\ln R/dN$, which are obtained from the second column through multiplication by 8.79. These figures therefore show the change in the resistance of mercury which would be produced by the three metals, assuming that the effect of the dissolved metal is due solely to the accompanying volume change. The fourth column gives the values of $d\ln R/dN$ obtained directly from our measurements, by finding the slope of the resistance curve at $N = 0$. These figures will vary somewhat according to the relative weight given to the measurements at the lowest concentration. The fifth column gives the values of $(d\ln R/dN)_{V'}$ namely, the fractional change in the resistance per gram-atom of dissolved metal when the average atomic volume is kept constant. These figures are obtained by subtracting the second column from the third.

TABLE IV

	$\frac{d \ln V'}{dN}$	$\frac{d \ln R}{dN}$ (calc.)	$\frac{d \ln R}{dN}$ (obs.)	$\left(\frac{d \ln R}{dN}\right)_{V'}$
Lithium	−0.534	−4.70	−0.82	+3.88
Sodium	−0.014	−0.12	+0.92	+1.04
Potassium	+0.643	+5.66	+2.73	−2.93

It is evident that when added at constant atomic volume lithium would increase and potassium decrease the resistance of mercury, the very reverse of that which happens at constant pressure. The parallelism between the figures of the second and the third columns is striking; we need not, however, consider the change in volume and the change in resistance to be directly related as cause to effect, but rather we shall regard them as concomitant effects of some condition in the immediate neighborhood of the dissolved particles, a condition which probably is closely connected with what is known as the solvation of the dissolved metal. The amount of this solvation or combination with the solvent undoubtedly increases in the same order as the electrical resistance, being least in the case of lithium and greatest in the case of potassium. Thus, to cite one of the most direct pieces of evidence, it is shown by Lewis and Keyes[8] that the heats of solution in mercury of lithium, sodium, and potassium are respectively 19,600, 19,800 and 26,000 calories.

In drawing attention to the difference between the phenomenon of conductivity in dilute amalgams and in dilute electrolytic solutions, it is only just to remark that, since we are considering solutions in a solvent which is itself a good conductor, the case is not entirely analogous to that of salts dissolved in a poor conductor like water, but rather to a solution of a salt in another molten salt, a system which has not as yet been intensively studied.

[1] Kraus, *J. Amer. Chem Soc.*, **29**, 1557 (1907); **30**, 653 (1908); **30**, 1197 (1908); **30**, 1323 (1908); **36**, 864 (1914).

[2] Lewis, Adams, and Lanman, *J. Amer. Chem. Soc.*, **37**, 2656 (1915).

[3] Bornemann, *Metallurgie*, **7**, 730 (1910); **9**, 473 (1912).

[4] Kraus, *Physic. Rev.*, Ser. 2, **4**, 159 (1914).

[5] Maey, *Zs. physik. Chem.*, **29**, 119 (1899).

[6] Bridgman, *Proc. Amer. Acad. Arts Sci.*, **44**, 221 (1909).

[7] Landolt, Börnstein, and Roth, *Tabellen*.

[8] Lewis and Keyes, *J. Amer. Chem. Soc.*, **35**, 340 (1913).

IDEATIONAL BEHAVIOR OF MONKEYS AND APES

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The reactive tendencies of two monkeys and a young orang utan have been studied by means of the method of multiple choices described in a previous communication to the Academy[1] and by certain supplementary methods.

Four multiple choice problems were presented: (1) the problem of choosing from among any group of mechanisms the one at the left; (2) the second from the right end; (3) alternately, the first at the left end and the first at the right end; (4) the middle mechanism.

Each of the three primates in question solved problem 1. One monkey (P. rhesus) required 70 trials; the other (P. irus), 132 trials. The ape succeeded only after 290 trials. The behavior of these three animals was most interesting and illuminating. P. irus was erratic, easily fatigued or discouraged, and apparently of low grade intelligence. P. rhesus, on the contrary, was alert, businesslike, intent on his task, and direct in his attack on experimental devices. The orang utan was childlike in his desire for assistance, as also in his resentment of annoyances or disappointments. He was given to settling down to a simple routine.

The accompanying figure 1 presents the curves of error for these animals as constructed from the data in connection with problem 1.

P. rhesus (Sobke) quickly and regularly eliminated mistakes and completely solved the problem. His disposition as well as his achievement, is pictured by the curve of errors.

P. irus (Skirrl) exhibited marked irregularities of performance, and the curve indicates his variable attention and effort as well as his slow progress toward success.

The orang utan (Julius) reacted uniquely, as his curve suggests. At the very outset, he developed a definite habit of response which, as it happened, was inadequate for the solution of the problem but yielded constantly 60% of correct first choices. The habit or reactive tendency was that of choosing each time the box nearest to the starting point.[2] Julius continued to use this method without variation for eight successive days. Then a break occurred, but after a few days he settled back into the old rut. At the end of 230 trials, it was decided to try to destroy the ape's unprofitable habit. This attempt was made by using

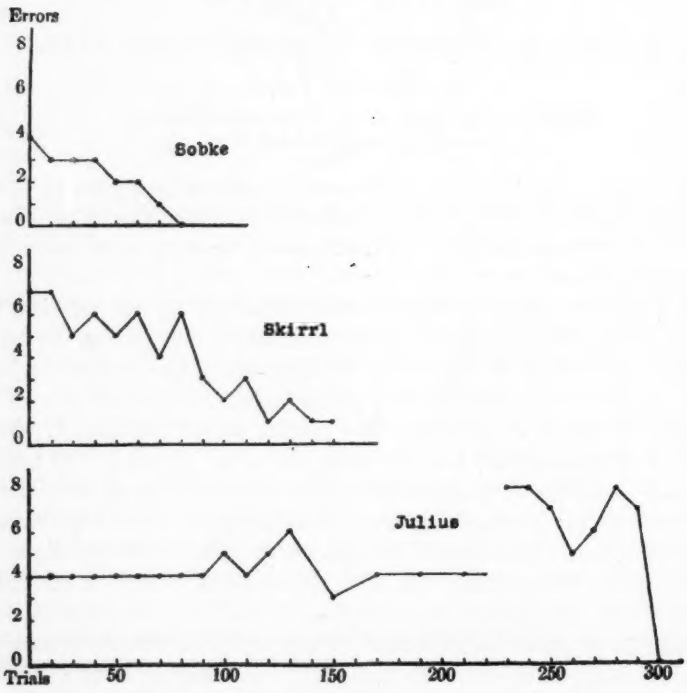

FIG. 1

as correct boxes only those to the left of the middle box of the series. The nearest box, in such case, was never the correct box. Consequently, this modification of method greatly increased, as the curve of errors shows, the number of mistakes.

For a few days after this change was made, no improvement in reaction appeared. On May 10, in a series of 10 trials, 7 were incorrect, but the following day and thereafter only correct choices appeared. Thus, suddenly and without warning, the ape solved his relational problem.

Is this the result of ideation? If not, what happened between the poor performance on May 10 and the perfect series on May 11? Because of varied results obtained in other experiments with this ape, I suspect that ideational processes developed.

The two monkeys succeeded in solving problem 2; the P. irus after 1070 trials, and the P. rhesus after 400 trials. The orang utan failed utterly, although he was given 1380 trials. Ultimately, he ceased to try to select the right box and followed the path of least resistance.

In addition to the method of multiple choices, the chiefly significant results of which cannot well be summarized, several supplementary methods of studying the adaptive behavior of monkeys and apes were employed. Chief among these are (1) a box stacking test; (2) a box and pole experiment; (3) a form of draw-in experiment.

The ape, although failing to stack boxes spontaneously in order to obtain a banana which was suspended from the roof of his cage, did so readily and skilfully when shown how to do it by the experimenter. His imitative activity was convincingly purposive. Previous to the opportunity to imitate the experimenter, he exhibited various methods of trying to get the banana. His attention was surprisingly constant, and his activity, although varied, was for the most part definitely directed toward the food. In the controlling influence of the prospective reward and in the precision of execution of his various acts, Julius differed markedly from the monkeys.

Neither monkey made systematic and sustained attempts to obtain the banana by the use of boxes. Neither imitated the experimenter and neither attended to the prospective reward more than a few seconds at a time. These statements indicate a vast gulf, psychologically, between monkey and ape.

In the box and pole experiment, the banana was so placed in the middle of a long box that it could be obtained only by the use of a pole. The ape quickly, of his own initiative and with few useless motions, succeeded in obtaining the food. The monkeys never succeeded in obtaining it by any method and failed to use the pole at all as a tool.

Similarly, in an experiment which gave the animals opportunity to obtain food by drawing it into the cage with a stick, the ape quickly and repeatedly adapted means to ends by using the stick, whereas the monkeys never once attempted to use it.

The specimen of P. irus (Skirrl) had a penchant for the manipulation of objects as tools. It is therefore surprising that he failed in the above experiment. When given a board, hammer and nails, he drove the nails into the board skilfully and persistently only to draw them out again and repeat the performance, for the activity was its own reward. In all probability, this use of hammer and nails was not imitative, since no other monkey or ape under observation showed any inclination to use them as did Skirrl. Quite as assiduously and with evident satisfaction, he used lock and key, and saw, or any other object which happened to fall into his hands. In the use of a saw, he persistently refused or failed to imitate the experimenter, but finally hit upon a use for the instrument which clearly gave him great satis-

faction. By holding it, teeth uppermost, with his feet and rubbing a nail or spike over the teeth rapidly, he succeeded in producing a noise which apparently delighted him. Skirrl, although pronounced feeble-minded on the basis of various studies of problem-solving ability and reactive tentencies, proved himself to be a mechanical genius.

The general conclusions which may be deduced from this limited experimental study of two monkeys and an orang utan are that the ape exhibits various forms of ideational behavior, whereas the reactive tendencies of monkeys are inferior in type and involve less adequate adaptation to factors remote in space or time. I suspect, from data now available, that both monkeys and apes experience ideas, and I believe that it will shortly be possible to offer convincing evidence of the functioning of representative processes in their behavior.

The original account of the results which have been summarized in this communication presents also a plan for a research station to be devoted to the study of the primates. It is pointed out that without scientific conscience we have permitted race after race of primitive man to disappear, unstudied by psychologist, sociologist, or anthropologist, or at best inadequately studied. The pertinent question of the comparative psychologist is "Are we also to permit the gorilla, chimpanzee, orang utan, and gibbon to disappear before we make them yield their incalculably valuable contribution to human enlightenment, welfare, and the general progress of science?"

[1] A new method of studying ideational and allied forms of behavior in man and other animals, these PROCEEDINGS, 2, 631, (1916).

[2] In the apparatus used for these observations, the boxes were placed in a straight line instead of on the arc of a circle. Consequently, the distance from the starting point increased from the center of the series toward the ends.

THE OSMOTIC PRESSURE AND LOWERING OF THE FREEZING-POINT OF MIXTURES OF SALTS WITH ONE ANOTHER AND WITH NON-ELECTROLYTES IN AQUEOUS SOLUTIONS

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In the work of this laboratory upon the abnormalities in behavior of salts in aqueous solutions with respect to their ionization, it seemed desirable to determine the effect of mixing salts with common ions. Since in this laboratory we have a potentiometer system which gives

temperature readings to 0.00005°, the work was carried out by the freezing-point method.

Freezing-point determinations at various concentrations were made upon solutions of mannite, erythrite, potassium iodate, sodium iodate, magnesium sulphate, potassium sulphate, barium chloride, and cobalt chloride, and upon mixtures of potassium chloride and potassium nitrate, potassium chloride and mannite, potassium and sodium sulphates, and of potassium and sodium iodates. The method used was similar to that of Adams, and the same apparatus was used. Most of the analyses for the determination of the concentration of the solutions, were made by the use of a Haber-Rayleigh-Zeiss water-interferometer.

The results are expressed most clearly in the form of curves, which

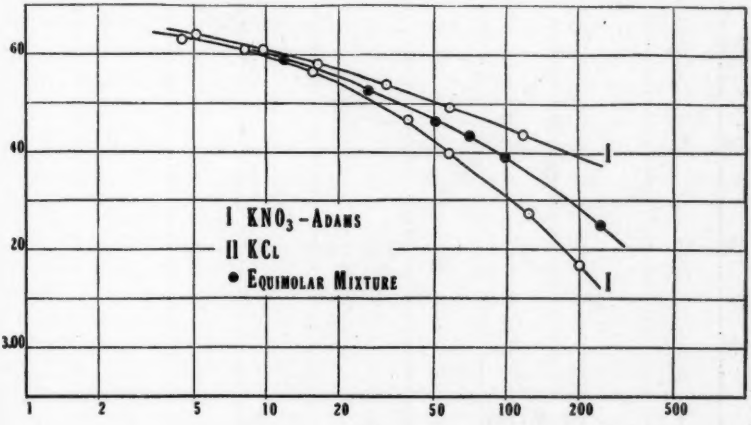

FIG. 1

are presented in figures 1–3. These figures show the values of the freezing-point lowerings divided by the equivalent concentrations ($\Delta T/N$) on the Y-axis, and the logarithms of the concentrations in milli-equivalents per liter on the X-axis. Figure 1 gives the set of curves for potassium nitrate, potassium chloride, and their equimolal mixture. The curve for the mixture will be seen to lie about half-way between those which represent the salts separately. Figure 2 gives the results for sodium iodate, a uni-univalent salt, and for magnesium sulphate, a bi-bivalent salt. Potassium iodate, and an equimolal mixture of it with sodium iodate were also studied, but the two curves are not given as they are almost coincident with that for sodium iodate. Figure 3 gives those for potassium sulphate, barium chloride, and cobaltous

chloride, three uni-bivalent salts. Lanthanum nitrate, a tri-univalent salt, was also investigated.

The general result obtained with the mixtures investigated up to the present time is that the lowering of the freezing-point of the mixture is

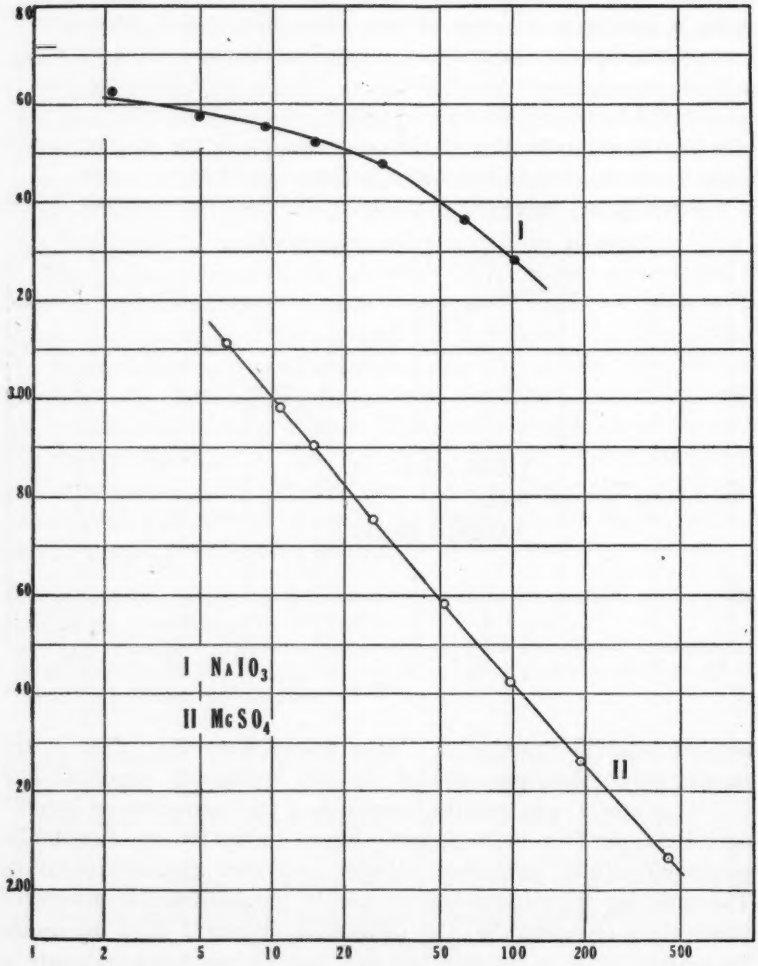

FIG. 2

very nearly that which would be calculated on the basis that each salt produces a lowering of the freezing-point proportional to its own concentration and to the mol-number (van't Hoff coefficient i) which it has

when present alone in a solution of the same total salt concentration. In the 1 : 1 mixtures the freezing-point curve for the mixture lies midway between the curves for the two salts taken separately. However, it would not be surprising if later results on other salts should show somewhat different relations; for the salts thus far used have been chosen because on the whole they act normally in other respects.

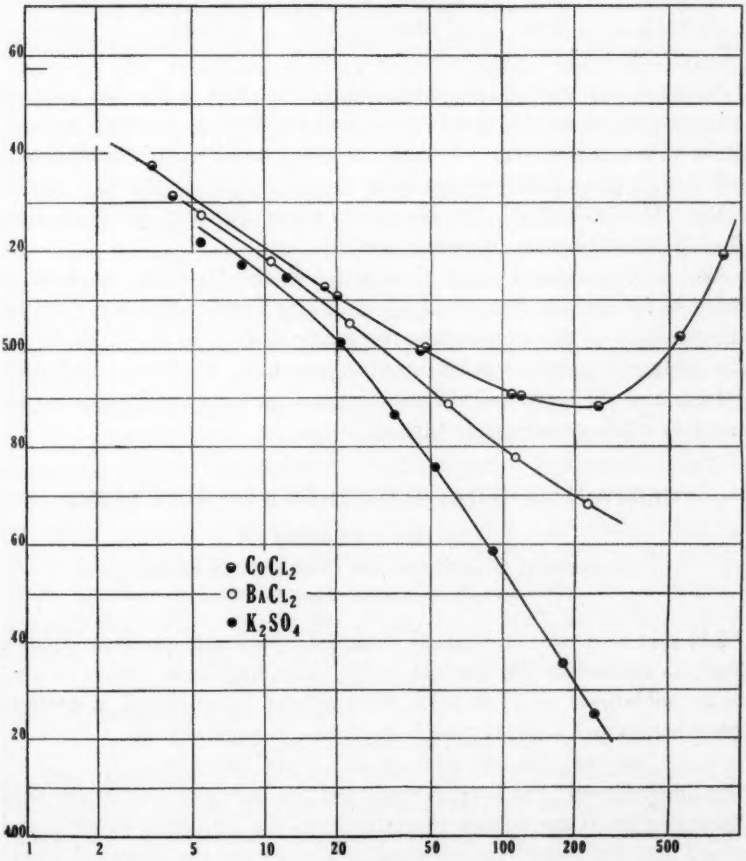

FIG. 3

The results obtained on a mixture of 1 mol of mannite and 2 mols of potassium chloride are given in the following table, which shows how closely the effect is additive. The 'deviation' given in the last column shows how much the sum of the freezing-point-lowerings caused by the separate components exceeds that observed for the mixture.

TABLE 1.

LOWERING OF THE FREEZING-POINT IN A MIXTURE OF MANNITE AND POTASSIUM CHLORIDE

CONC. MANNITE	CONC. KCl	MIXTURE	FREEZING-POINT LOWERING		DEVIATION
			Mannite	KCl alone	
0.00493	0.00987	0.04479	0.00927	0.03557	0.00005
0.01071	0.02153	0.09676	0.02012	0.07670	0.00006
0.02183	0.04367	0.19400	0.04061	0.15343	0.00004
0.04067	0.08134	0.35700	0.0757	0.2813	0.0000

So far as the writers have been able to find, this is the first work on mixtures of salts which has been carried out with an accurate temperature measuring system. One set of measurements on mixtures of a salt with a non-electrolyte has been carried out by Osaka [*Zs. physik. Chem.*, **41**, 560 (1902)], but his results show a greater deviation than that illustrated by the preceding table.

We wish to express our indebtedness to the National Academy of Sciences for a grant from the Wolcott Gibbs Fund, which was used for the purchase of the temperature measuring system, to W. P. White for the design of a special potentiometer, and to L. H. Adams and John Johnston of the Geophysical Laboratory of the Carnegie Institution for the loan of the freezing-point apparatus.

CERTAIN GENERAL PROPERTIES OF FUNCTIONS

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Let $g(x)$ be a real, one-valued, bounded, continuous or discontinuous function defined in the interval (a, b). The functional values of $g(x)$ *in the subinterval* (α, β) of (a, b) have a least upper-bound, a greatest lower-bound and a saltus, which we denote respectively by

$$u(g, \alpha\beta),\ l(g, \alpha\beta) \text{ and } s(g, \alpha\beta) = u(g, \alpha\beta) - l(g, \alpha\beta).$$

The upper-bound, the lower-bound[1] and the saltus of $g(x)$ *at the fixed point* x of (a, b) are defined respectively as the (greatest) lower-bound of $u(g, \alpha\beta)$, the (least) upper-bound of $l(g, \alpha\beta)$ and the (greatest) lower-bound of $s(g, \alpha\beta)$ for all possible subintervals (α, β) of (a, b) that contain x as interior point.[2] With the given function $g(x)$, there are thus associated three new functions of x, *the upper-bound function*, *the lower-bound function* and *the saltus function*, which we denote by

$$u(g, x),\ l(g, x) \text{ and } s(g, x)$$

respectively.[3]

It is seen that

$$s(g, x) \equiv u(g, x) - l(g, x).$$

Let us, for the sake of brevity, write

$$s(g, x) \equiv s'(x),\ s(s', x) \equiv s''(x),\ s(s'', x) \equiv s'''(x), \ldots .$$

Sierpiński[4] has proved the

Theorem. $s''(x) \equiv s'''(x) \equiv s^{IV}(x) \ldots .$

The chief aim of the present paper is to communicate a number of companion propositions to Sierpiński's theorem. The new results are based on the definition of other types of saltus, which immediately suggest themselves and arise from the one described above, when certain specified subsets of the range of the independent variable may be neglected.

The first new type arises when *finite* subsets may be neglected. For every subinterval (α, β) of (a, b), there evidently exists a number, which we denote by $u_f(g, \alpha\beta)$, uniquely characterized by the following double property:[5] For every $\epsilon > 0$, on the one hand, the set of points of the interval (α, β) for which $g(x) > u_f(g, \alpha\beta) + \epsilon$ is finite, while on the other hand, there exists an infinite set of points of (α, β) at which $g(x) > u_f(g, \alpha\beta) - \epsilon$. This number $u_f(g, \alpha\beta)$ is the lower-bound of all possible upper-bounds that $g(x)$ may have in the interval (α, β), in case a finite set of points may be neglected. Likewise, there is a number, which we denote by $l_f(g, \alpha\beta)$ characterized by the property that for every $\epsilon > 0$, the set of points of (α, β) where $g(x) < l_f(g, \alpha\beta) - \epsilon$ is finite, whereas, the set of points of (α, β) where $g(x) < l_f(g, \alpha\beta) + \epsilon$ is infinite. $l_f(g, \alpha\beta)$ is the upper-bound of all possible lower-bounds of $g(x)$ in (α, β), when a finite number of points may be neglected. Finally, we denote by $s_f(g, \alpha\beta)$ the lower-bound of the saltus of $g(x)$ in (α, β), in case a finite number of points may be neglected. Evidently

$$s_f(g, \alpha\beta) = u_f(g, \alpha\beta) - l_f(g, \alpha\beta).$$

We shall designate the numbers

$$u_f(g, \alpha\beta),\ l_f(g, \alpha\beta) \text{ and } s_f(g, \alpha\beta)$$

as '*the f-upper-bound*,' '*the f-lower-bound*' and '*the f-saltus*' of $g(x)$ *in the interval* (α, β). As in the case where no point may be neglected, we now define '*the f-upper-bound*,' '*the f-lower-bound*,' and '*the f-saltus*' of $g(x)$ *at the fixed point* x of (a, b), as the lower-bound of $u_f(g, \alpha\beta)$, the upper-bound of $l_f(g, \alpha\beta)$ and the lower-bound of $s_f(g, \alpha\beta)$ for all possible subintervals (α, β) of (a, b) that contain x as interior point. With the given function $g(x)$, we have thus associated '*the f-upper-bound function*,' '*the f-lower-bound function*' and '*the f-saltus function*,' which we denote by

$$u_f(g, x), l_f(g, x) \text{ and } s_f(g, x)$$

respectively.

In the second place, the subsets that may be neglected are *denumerable*. As before, there exists a number, which we denote by $u_d(g, \alpha\beta)$, uniquely characterized by the property that, for every $\epsilon > 0$, the set of points of (α, β) where $g(x) > u_d(g, \alpha\beta) + \epsilon$ is denumerable, whereas the set of points where $g(x) > u_d(g, \alpha\beta) - \epsilon$ is non-denumerable; this number $u_d(g, \alpha\beta)$ we call '*the d-upper-bound*' of $g(x)$ in (α, β). Precisely as before we define the related numbers

$$l_d(g, \alpha\beta), s_d(g, \alpha\beta), u_d(g, x), l_d(g, x)$$

and '*the d-saltus function*' $s_d(g, x)$.

In the third place, '*exhaustible*' sets (i.e., sets of first category[6]) may be neglected. We then obtain '*the e-saltus function*' $s_e(g, x)$, together with the related numbers.

Finally, sets of (Lebesgue) *zero measure* may be neglected. We then obtain '*the z-saltus function*' $s_z(g, x)$, together with the related functions.

As in the case where no point may be neglected, we write

$$s_f(g, x) \equiv s_f'(x), s_f(s_f', x) \equiv s_f''(x), s_f(s_f'', x) \equiv s_f'''(x), \ldots;$$

and similarly for the d-saltus, the e-saltus and the z-saltus functions.

Having defined the new types of saltus we had in view, we may now state the corresponding analogues of Sierpinski's theorem. The most interesting and least obvious results are the following two theorems.

Theorem. $s_d'''(x) \equiv s_d^{IV}(x) \equiv s_d^{V}(x) \equiv \ldots$

Theorem. $s_z'''(x) \equiv s_z^{IV}(x) \equiv s_z^{V}(x) \equiv \ldots$

Moreover, as examples show, $s_d''(x)$ and $s_z''(x)$ may be different from $s_d'''(x)$ and $s_z'''(x)$ respectively.

In the case of the f-saltus, the functions $s_f^{(n)}(x)$ $(n = 1, 2, \ldots)$ *may all be different.*

In the case of the e-saltus, while $s_e''(x)$ may be $\neq s_e'''(x)$, we have

Theorem. $s_e'''(x) \equiv 0.$

A generalization of our result for the d-saltus is as follows:

Theorem. If $s'_{\aleph}(x), s''_{\aleph}(x), s'''_{\aleph}(x) \ldots$ *represent the successive saltus functions that arise when,* instead of neglecting denumerable sets (i.e., sets of cardinal number $\aleph_0$), *we neglect sets of cardinal number* $\aleph$, *where* $\aleph$ *is any cardinal number* $< c$, the cardinal number of the continuum, *then*

$$s'''_{\aleph}(x) \equiv s^{IV}_{\aleph}(x) \equiv s^{V}_{\aleph}(x) \equiv \ldots$$

Because of our negative result in the case of the f-saltus, we are naturally led to define $s_f^{(\beta)}(x)$ for transfinite β's. Our result will show that it is sufficient to confine ourselves to transfinite numbers belonging to Cantor's second class. If β is not a limiting number, $\beta - 1$ exists, and

we define $s_f^{(\beta)}(x)$ as equal to $s_f(s_f^{(\beta-1)}, x)$. For our purpose, therefore, all we have to do now is to define $s_f^{(\beta)}(x)$, in case β is a limiting number, in terms of the functions $s_f^{(\nu)}(x)$, where $\nu < \beta$. This we do simply by means of the equation

$$s_f^{(\beta)}(x) = \lim_{\nu_n \to \beta} s_f^{(\nu_n)}(x),$$

where $\{\nu_n\}$ is a sequence of numbers less than β. It is seen that this limit always exists and is independent of the particularly chosen sequence $\{\nu_n\}$.

Our positive result for the case of the f-saltus may now be stated as follows:

Theorem. There exists a number β of the first or the second class, such that

$$s_f^{(\beta)}(x) \equiv s_f^{(\beta+1)}(x).$$

Furthermore, it is shown by means of an example, that *if β is a given number of the first or the second class, then the functions $s_f^{(\nu)}(x)$ $(1 \leqq \nu \leqq \beta)$ may all be different, whereas $s_f^{(\beta)}(x) \equiv s_f^{(\beta+1)}(x)$.*

The following interesting connection exists between the d-saltus and the f-saltus.

Theorem. For every function $g(x)$ for which $s_f^{(\beta)}(x) \equiv s_f^{(\beta+1)}(x)$ —— and according to the preceding theorem there always exists such a β of the first or the second class ——, *we have*

$$s_d(s_f'', x) \equiv s_f^{(\beta)}(x).$$

The results may be easily extended to the case of many-valued, bounded, or unbounded functions of several variables, or of infinitely many variables; and by means of simple postulate systems, to more abstract situations.

The above is essentially the introduction of a paper, which is to be offered to the *Annals of Mathematics*.

[1] Throughout the paper, we use the expressions, 'the upper-bound' and 'the lower-bound,' in the sense of 'the least upper-bound' and 'the greatest lower-bound,' respectively.

[2] Of course, it will be understood, that in case $x = a, b$—and only then—we permit α, β to coincide with x. This remark applies also to similar situations below.

[3] The functions $u(g, x)$ and $l(g, x)$ are often, though not quite unobjectionably, called the 'maximum' and the 'minimum' functions belonging to $g(x)$. Cf., for example, Hobson, *The Theory of Functions of a Real Variable* (1907), art. 180.

[4] *Bull. Acad. Sci., Cracovie* (1910), 633–634.

[5] Cf. Baire, *Acta Mathematica*, 30, 21 and 22 (1906).

[6] Cf. Denjoy, *J. math. Paris*, Ser. 7, 1, 122–125 (1915).

SPHENACODON MARSH, A PERMOCARBONIFEROUS THEROMORPH REPTILE FROM NEW MEXICO

By Samuel W. Williston

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Thirty-eight years ago, O. C. Marsh gave the name *Sphenacodon ferox* to some jaws and vertebrae collected by David A. Baldwin near Arroya de Agua in Rio Arriba County, New Mexico. From his brief description it was suspected that the form was nearly allied to the remarkable reptiles known as *Dimetrodon* Cope, from the Permian of Texas, and a study of the type collections in the Yale Museum enabled me a few years ago to confirm the suspicion. The locality whence the type specimens came had almost been forgotten till five years ago, when Mr. Paul Miller, Prof. E. C. Case and I rediscovered the original bone-bed of Baldwin about a mile and a half above the confluence of the Poleo creek with the Puerco, and near the Mexican village of Arroya de Agua. Numerous specimens were obtained from this deposit, fixing the identity of the forms with those of other remains obtained from a bone-bed in the same horizon and a half mile nearer the mouth of the Poleo. From this bone-bed or 'bone-quarry,' discovered by Mr. Miller, numerous isolated bones of *Sphenacodon* and *Ophiacodon* Marsh, together with a very perfect skeleton of the latter, were obtained, but lack of time prevented a thorough exploitation of the deposit.

The past season my son, Samuel H. Williston, and I spent a few weeks in the same region, securing some very interesting and important specimens, a detailed description of which will be published later, including the material upon which the accompanying figure is based.

The 'Miller bone-bed' is in a hard, dark brown clay, which is worked with some difficulty because of the heavy embankment over it. It extends for about 100 feet along the foot of the high hills bordering the Poleo, and bids fair to yield not a few more good skeletons. About 20 feet east of the spot that yielded the remarkable skeleton of *Ophiacodon* that has been described, a femur of *Ophiacodon* was observed protruding from the excavation made by us in 1911. Upon following it up, two skeletons were discovered, one of *Ophiacodon*, lying immediately upon another of *Sphenacodon*, with their ends reversed. The extreme tip of the skull of *Sphenacodon* had been removed and lost in our previous excavations. It is altogether possible that I am the one who is responsible for the mutilation, but I am quite willing to share the responsibility with Mr. Miller and Prof. Case!

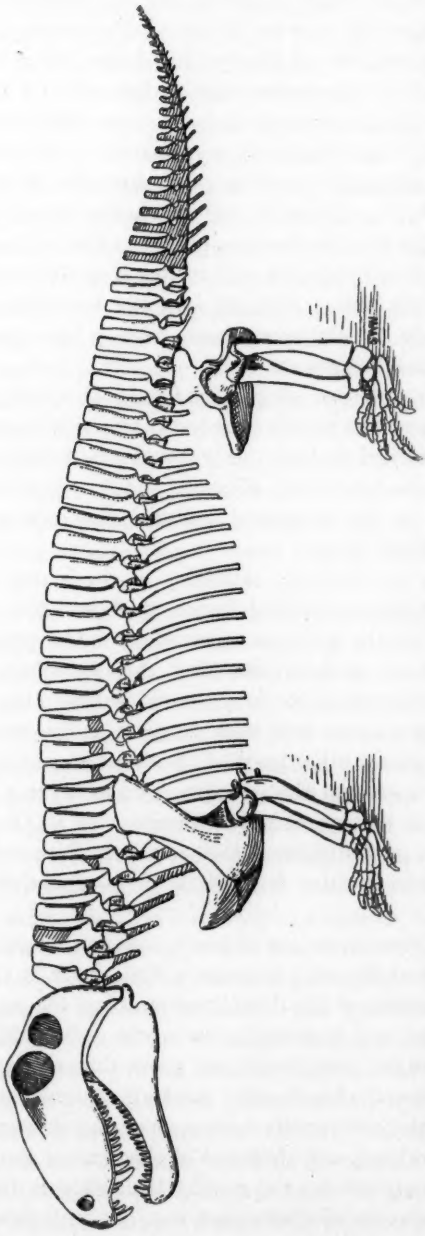

FIG. 1.—SPHENACODON MARSH, RESTORATION OF SKELETON, ONE-EIGHTH NATURAL SIZE. THE SKELETON IS REPRESENTED IN A WALKING POSTURE.

Otherwise the skull is very complete and but little distorted. Connected with the skull was a series of twenty-five presacral, three sacral and four caudal vertebrae, all closely united save for a break back of the eleventh vertebra, where there was an interval of a few inches, in which was found a single centrum and two connected spines, fixing the series as not less than twenty-seven presacral vertebrae. An additional spine, or twenty-eight in all was collected with the specimen, but inasmuch as isolated vertebrae are not rare in the deposit it is possible that the twenty-eighth spine does not belong in this series, but its close agreement with the adjoining spines makes it probable that it does, making twenty-eight presacral in all. In the accompanying restoration, however, only twenty-seven have been given, the number so commonly found in allied genera.

In collecting the vertebrae lying in the loose shales near the surface of the embankment, some fragments were lost connecting the spines, which, however, were attached to each other by the thin hard matrix with which all the bones were covered. These missing parts, which will doubtless be recovered in the excavated material next season, have been represented by oblique lines.

With this series of vertebrae, extending to the fourth caudal, were found parts of the girdles and limb bones which had been more or less lost by exposure, or the previous excavations. The preserved parts, however, are sufficient to determine their close agreement in size and characters with more perfect specimens found isolated near by. Of the feet nothing has been determined with certainty in this quarry, but the general agreement of the other parts of the skeleton with corresponding parts of *Dimetrodon*—except the vertebrae—make it practically certain that these parts are not appreciably different. As in *Dimetrodon*, the tail is, for the most part, unknown, and, as also in *Dimetrodon* the parts actually preserved in position leave little or no doubt of its relative shortness.

The spines of *Sphenacodon* are of nearly uniform length to the base of the tail. Those of the neck increase a little, both in thickness and length to the beginning of the dorsal region above the scapula, where they are the longest and stoutest in the whole series. They decrease very slightly in length posteriorly and grow thinner and less stout. With the first presacral they become markedly thinner and narrower and with the caudals grow rapidly more slender and shorter, leaving little doubt of the weakness and shortness of this part of the body. The vertebrae here also are shorter and smaller than those in front of them.

The ends of the cervical ribs have been lost, but with those exceptions

they are preserved throughout the column, and not a few of them have been mended more or less completely. They are relatively slender for the size of the animal, and but little curved. Their unusual length was unexpected. The rib of the fifteenth vertebrae, for instance, measures more than ten inches. Inasmuch as the depth of the body is fixed by the girdles these ribs show decisively a broad body. The width back of the fore-legs could not have been less than twenty inches, or nearly a half of the length of the body to the sacrum, and may have been more. The length of the twenty-second, or fifth presacral, rib is seven inches. In the cervical and dorsal region they articulate by two well separated heads, the tubercle with the diapophysis, which is prominent, the head with the intercentral space. Near the middle of the back the broad head is less markedly dichocephalous, and their movability was less. With the seventh or eighth presacral they begin to show sutural union with the diapophysis and a facet on the front end of the centrum. At the fifth presacral the sutural union is obliterated and the ribs were fixed and immovable. As in *Dimetrodon*, the ribs extend back quite to the sacrum, the first presacral pair having an expanse of not less than six inches. Perhaps this unusually broad body is another reason for the short tail.

In a previous paper it was observed that the articular surface at the proximal end of the humerus in *Ophiacodon* has a spiral form, as is usual in the pelycosaurs, and that, in life the humerus could not have been depressed much below the horizontal without dislocation from the socket. Mr. Watson has called attention to this peculiarity of the American theromorphs and cotylosaurs, and has suggested that it explains the unusual expansions of the ends of this bone in these animals. It has been assumed that the remarkably broad and stout humeri of the cotylosaurs and pelycosaurs meant burrowing habits, but I have shown the error of this assumption in the fact, that, for the most part, the front legs are short, the fingers scarcely reaching as far forward as the end of the beak. Certainly an animal that could not reach in front of its nose would have difficulty in excavating a hole for the body to enter, unless it temporarily removed its head! The legs were carried, for the most part, with the elbow bent at a right angle, and the movement of the foot backward and forward in this position would account for the spiral motion in the glenoid socket. Furthermore, such a position of the limbs would require, for the support of the body, strong and broad muscular attachments on the humeri, a sufficient explanation of their shape.

Nearly every detail of the skull has been worked out and will be described and illustrated later. Suffice it to say here that the presence

of quadratojugals, dermosupraoccipitals and tabulars has been definitely determined, and the supratemporals almost as definitely, thus giving to the genus nearly every skull element found in the most primitive cotylosaurs. The mandibles may be a little less slender and there may be fewer teeth but one can say with assurance that were an isolated skull of *Sphenacodon* found in Texas it would be referred unhesitatingly to *Dimetrodon*. And this similarity extends to other parts of the skeleton, with the exception of the spines of the vertebrae.

Many and various have been the conjectures offered to explain the extraordinary spines in *Dimetrodon*. In my opinion nothing better has been suggested than that of Professor Case, namely, that they represent an ornamental or senile character of the race, of no profound importance in the life economy of the animals. Certainly, as I have previously observed, if the spines of *Dimetrodon* had been of important use to their possessors they must have produced correlated differences in other parts of the skeleton. The differences in the spines have no more than a generic value.

There are doubtless several species of *Sphenacodon* in the New Mexican beds, but the known remains from the Baldwin and Miller bonebeds seem all to belong to one species. From different horizons on the Puerco, however, large specimens are known, now preserved in the Yale Museum. The present specimen, which doubtless belongs to *S. ferox* Marsh, was nearly five feet long as figured. The Yale specimens indicate a form one-half larger, or about seven and a half feet in length, or of about the size of most specimens referred to *Dimetrodon incisivus*. *Sphenacodon* is definitely known only from the valley of the Puerco and its tributaries in New Mexico; not a fragment of it has been found in the El Cobre deposits scarcely a score of miles away. However, there are specimens in the Chicago collection from Texas that suggest very strongly its occurrence there, but definite proof is lacking.

ON VOLUME IN BIOLOGY

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In one respect this subject is time-honored. Herbert Spencer and many others since his day have recognized the biological importance of the principle of similitude. Bulk increases as the cube of length; surface as the square. Hence the limitation of the size of cells, the

minute canalization of the body, and the prodigious jumps of the flea, as well as the variation in metabolism with the size of the organism. Yet even this subject is by no means exhausted. For example (a fact which appears to be of some importance in describing the internal regulation of temperature) the difference in temperature between center and surface of a sphere which is producing heat uniformly throughout its whole mass, when equilibrium has been established with a surrounding liquid medium of constant temperature, is proportional to the square of the radius.[1]

But apart from this great principle and certain superficial discussions of the nature of oedema and similar phenomena, the regulation of volume has remained without any physico-chemical analysis. Yet, from the standpoint of physical science, this is perhaps the most universal and fundamental of all organic regulations. I believe that this strange neglect may be traced to three facts. In the first place, the chemist is accustomed to vary the volume of his systems to suit his convenience. This is a justifiable practice, because, if the phases are so large that capillary phenomena may be disregarded, and so small that gravity need not be taken into account, the division of a phase into two parts does not change its energy. Thus, volume hardly enters into our calculations except as an indirect expression for that which is regarded as the true variable, viz., concentration. This, however, is to disregard the real question as it presents itself in biology. Secondly, ***when equilibrium has been established*** in a heterogeneous system, as Willard Gibbs rigorously proved, the volume of the phases—capillary and gravitational phenomena being absent—is not relevant to the state of the system. But it may be at once observed, first, that until equilibrium has been attained the volume is of great moment, and, secondly, that equilibrium is never attained within the organism. Finally, the ordinary conception of the process of diffusion is based upon a mathematical discussion, which, though leading to a consistent description of the phenomena, is nevertheless a false representation of the actual occurrences. And nearly all physiological changes of volume depend upon diffusion.

Contrary to a general though vague belief, the regulation of volume is theoretically independent of osmotic pressure regulation. For example, if a kidney produces a liter of urine of the same freezing point as blood, it must have diminished the volume of the body and left the osmotic pressure sensibly unchanged.

For the purpose of discussion, the activity of the kidney may be reduced to the following fiction: First there must be an excretion of all

the dissolved constituents of blood plasma, including water itself, in such amounts as to bring the composition of the blood in all respects to a hypothetical normal composition; secondly, a certain portion of this normal plasma, minus the colloids, must be removed in order to regulate the volume.

Statistically the volume of the urine must vary with the magnitude of the volume regulation, although, in particular cases, it need bear no relation to this quantity. Now sodium chloride is the principal constituent of blood plasma. Hence, statistically the ratio Δ: NaCl (i.e. the ratio of freezing point depression to sodium chloride concentration in urine) will be small when the volume is large, and large when the volume is small. Thus we arrive at a theoretical deduction *a priori* of Korányi's coefficient.[2] This coefficient tells us, therefore, nothing about the mode of action of the kidney mechanism. It has no bearing on the question of the functions of glomeruli and tubules. For the ratio is seen to be, as existing evidence proves, necessarily liable to indefinite fluctuations in particular cases. There is involved merely a statistical truth, expressing the conditions under which any kidney must operate in case sodium chloride is the chief constituent of the blood.

The practical importance of this theoretical discrimination of volume regulation from the excretion of the several urinary constituents appears to be established by the fact that in pathological conditions the daily volume of urine may be constant during variations in amounts of water or salt ingested, even when such experiments lead to fluctuations in the physico-chemical properties of the urine.[3] For this shows that the regulation of volume may be deranged more or less independently of the proper excretory functions.

If the final stage of volume regulation has been neglected, the intermediate stages have been generally misconceived. Neither the swelling of colloids nor the pressure which results from osmosis can furnish the basis for an analysis of such phenomena. In their stead we must turn to the kinetic theory and to Willard Gibbs' thermodynamics. But it should be first remarked that osmotic 'pressure' and colloidal swelling 'pressure' hardly act as important sources of mechanical tension, in the living organism. Even oedema involves very small magnitudes of such pressures. Secondly, changes in volume merely consist in the passage of material from one phase to another (except in so far as physical and chemical changes within a phase may produce very slight fluctuations in volume). Finally, apart from the operation of special secretory mechanisms which we do not understand, such processes

consist in the diffusion through phases and across interfaces from points of higher to points of lower potential. In the internal phenomena no less than in the exchanges with the environment, and in the internal phenomena of a single phase no less than in the heterogeneous process, water is quite as much in question as the dissolved substances.

This fact has been generally overlooked, by the physicists even more than by the physiologists. We may consider a simple diffusion experiment in which a layer of water is placed above a layer of sugar solution. It is true that the sugar must diffuse up into the water, but it is also true that the water must diffuse down into the solution. Yet the phenomena of diffusion have always been discussed with the help of the mathematical theory of heat conduction as exactly defined by Fourier. Thus Fick's theory of diffusion overlooks the rôle of the solvent. This has been possible because the process takes place *as if* the solvent were inert and the dissolved substance possessed a higher diffusibility. But the diffusion of the solvent is probably greater than that of the solute, in that water is, with a few exceptions, the most diffusible of substances. In their neglect of the relativity of motion, contemporary accounts of diffusion involve an old fallacy that occurs even in the astronomy of Ptolemy.

It may perhaps be objected that throughout the organism water exists at a uniform potential. This, however, is both untrue and beside the point. For, if two phases are free to exchange material, an exchange involving all their components will take place unless, at the outset, all their components possess the same potential in both phases. Thus, as Höber[4] has shown, isotonic solutions of sodium chloride and magnesium sulphate change in volume when brought into contact. For the chloride diffuses faster than the sulphate. Thus the sulphate solution becomes more concentrated and, as a result, water diffuses into it from the chloride solution. In like manner differences of pressure and of temperature influence the potential of water and of all dissolved substances. Finally, the processes of metabolism are continually altering the concentrations of solutions, and therefore the potential of water.

When these facts are taken into account, it becomes clear that the chief physical factor in the internal regulation of volume is water, through its distribution between the infinite assemblage of phases which make up the organism. The general concepts of the phase rule reveal the several elements of this process—except those which depend upon so-called selective activities—but the physical theory of diffusion, and therefore the whole kinetic description, has been developed from a

false representation of the process, which neglects the movements of water itself. Only when this is immediately evident, as in osmotic phenomena, is it at all taken into account. But even here the current explanations are often incomplete. And the general theory of the diffusion of water is almost useless for the purposes of physiology. Yet there seems to be no reason to doubt that, in the organism, this is the most important process of diffusion.

[1] I am indebted to Prof. W. E. Byerly for kindly calculating the value of this difference which is $p/k.r^2/6$, where p is rate of heat production, k conductivity, and r the radius.

[2] A. v. Korányi, *Zs. Klin. Medizin*, 33, 1892, and Korányi und Richter, *Physikalische Chemie und Medizin*, Leipzig, 1908, 2, pp. 133–224.

[3] *Ibid.*, pp. 165, 166.

[4] *Pflüger's Archiv*, 74, 225 (1899).